VOL. XLVI SEPTEMBER, 1911 No. 3

AMERICAN

CHEMICAL JOURNAL

# THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC ZINC COMPOUNDS

## [SECOND COMMUNICATION]

BY E. P. KOHLER, G. L. HERITAGE AND A. L. MACLEOD

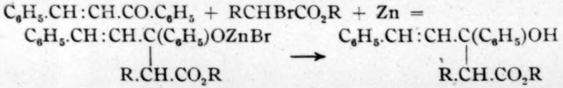
In the first paper[1] on this subject we published the results that were obtained by treating a variety of unsaturated compounds with zinc and bromacetic esters. We showed that a number of unsaturated ketones that form only saturated compounds when treated with Grignard reagents give unsaturated $\beta$-hydroxy esters when they react with zinc and bromacetic ester; and that ketones like benzaldesoxybenzoin and benzalacetomesitylene, which have an exceptionally unreactive carbonyl group, do not react with the zinc derivatives at all, although they give an excellent yield of 1,4-addition product with Grignard reagents. From these results we concluded that the mode of addition of organic zinc compounds derived from $\alpha$-brom esters is different from that of any Grignard reagent that has hitherto been used.

Our later experiments show that this conclusion should have been confined to the zinc derivatives of bromacetic esters. For while zinc bromacetates appear to form only 1,2-addition products with all kinds of unsaturated compounds, the zinc compounds obtained from other α-brom esters behave differently. Our work on the subject is not nearly completed, but in order to avoid misconceptions we think it best to indicate the character of the results by publishing an account of our experiments with one unsaturated ketone—benzalacetophenone.

---

[1] THIS JOURNAL, **43**, 475.

The product obtained by heating a benzene solution of benzalacetophenone and an α-brom ester may contain three classes of substances: zinc compounds that give unsaturated hydroxy esters when treated with an acid, zinc compounds that, on treatment with acid, give saturated ketonic esters, and unsaturated lactones. The first class of zinc compounds is evidently the result of 1,2-addition to carbonyl:

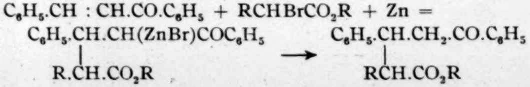


$$C_6H_5.CH{:}CH.CO.C_6H_5 + RCHBrCO_2R + Zn =$$
$$\begin{array}{c}C_6H_5.CH{:}CH.C(C_6H_5)OZnBr\\ |\\ R.CH.CO_2R\end{array} \longrightarrow \begin{array}{c}C_6H_5.CH{:}CH.C(C_6H_5)OH\\ |\\ R.CH.CO_2R\end{array}$$

More than one compound of this class may be formed because these substances contain both double linkages and dissimilar asymmetric carbon atoms. Stereoisomeric esters are frequently obtained.

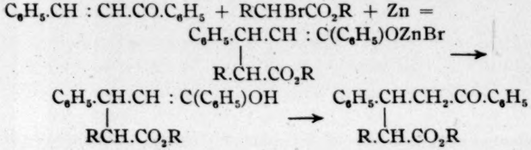
The second class might be formed either by 1,2-addition to the ethylene linkage, or by 1,4-addition to the conjugated system C : C.C : O:

I.



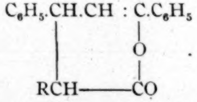
$$C_6H_5.CH : CH.CO.C_6H_5 + RCHBrCO_2R + Zn =$$
$$\begin{array}{c}C_6H_5.CH.CH(ZnBr)COC_6H_5\\ |\\ R.CH.CO_2R\end{array} \longrightarrow \begin{array}{c}C_6H_5.CH.CH_2.CO.C_6H_5\\ |\\ RCH.CO_2R\end{array}$$

II.

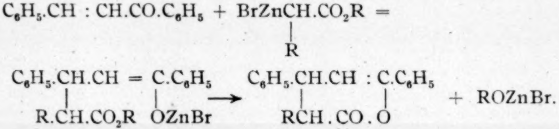


$$C_6H_5.CH : CH.CO.C_6H_5 + RCHBrCO_2R + Zn =$$
$$\begin{array}{c}C_6H_5.CH.CH : C(C_6H_5)OZnBr\\ |\\ R.CH.CO_2R\end{array} \longrightarrow$$
$$\begin{array}{c}C_6H_5.CH.CH : C(C_6H_5)OH\\ |\\ RCH.CO_2R\end{array} \longrightarrow \begin{array}{c}C_6H_5.CH.CH_2.CO.C_6H_5\\ |\\ R.CH.CO_2R\end{array}$$

The character of the unsaturated lactones proves that the second interpretation is correct. When these lactones are treated with sodium carbonate they give the same ketonic acids that result from the hydrolysis of the esters obtained from the second class of zinc compounds. They are therefore δ-lactones, as represented by the formula



The relative amount of lactones formed from a given brom ester varies with the conditions—concentration, length of heating, and other factors that cannot be sharply defined. As the lactones can be separated from the benzene solution containing all the products of the reaction without treating this solution either with water or acids, they must be formed directly from a zinc compound. They, therefore, supply excellent proof that the second class of zinc compounds is due to 1,4-addition:



Stereoisomerism is possible also in the case of the second class of zinc compounds and in that of the lactones.

It is clear, now, that the mode of addition of organic zinc compounds, derived from α-brom esters, to unsaturated compounds containing the conjugated system C : C.C : O is precisely the same as that of organic magnesium derivatives to the same class of substances. The final result depends upon the character of the unsaturated compound as well as that of the ester from which the metallic derivative is made. In most cases both 1,4- and 1,2-addition take place in the same reaction, and in order to ascertain the factors that influence the mode of addition it is necessary to find some method for estimating the relative amounts of 1,2- and 1,4-addition products in a mixture.

The oxidation method used with the corresponding products obtained from Grignard reagents was found inapplicable, because the lactones are almost as easily oxidized by permanganate as the unsaturated hydroxy esters, and the method failed even when, by working in very dilute solution, lactone formation was prevented, because the ketonic esters are oxidized with sufficient rapidity to vitiate the results. An attempt to determine the relative amounts by titration with a standard solution of bromine gave no better results. The hydroxy esters rapidly combine with bromine at —20°, and while the pure ketonic esters do not react with bromine at this temperature, in a mixture of the two both are attacked—probably because a small quantity of hydrobromic acid acts as a catalyst in the substitution of bromine in the $\alpha$-position in ketones.

The best method that we have been able to find up to this time consists in heating the mixture, containing all of the products, with a solution of sodium carbonate in a current of steam. By this procedure the unsaturated lactone and ketonic ester are gradually dissolved as sodium salt of the ketonic acid. The hydroxy ester is also hydrolyzed, but the process takes place very slowly and in most cases the resulting acid is decomposed almost as fast as it is formed. The acid obtained by acidifying the resulting solution was dried, weighed and regarded as ketonic acid due to 1,4-addition. The method does not give accurate results for two reasons: the ketonic acid is decomposed, very slowly and in variable quantities, into unsaturated compounds and fatty acids, and small, variable quantities of hydroxy acid remain undecomposed and are weighed as ketonic acid. These errors are in opposite directions, and from our whole experience with the method we estimate that our error does not exceed 10 per cent. The following results, obtained with benzalacetophenone, show how the results vary with the character of the brom ester:

| | Per cent. of 1,2-addition | Per cent. of 1,4-addition |
|---|---|---|
| $Br.CH_2.CO_2CH_3$ | 100 | 0 |
| $BrCH(CH_3)CO_2CH_3$ | 55 | 45 |
| $BrCH(C_2H_5)CO_2CH_3$ | 50 | 50 |
| $BrC(CH_3)_2CO_2CH_3$ | 0 | 100 |
| $BrCH(CO_2CH_3)_2$ | 0 | 100 |

The significance of these results for the interpretation of unsaturation will be discussed in a later paper dealing with a greater variety of unsaturated compounds.

## EXPERIMENTAL PART

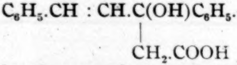
The reactions between unsaturated compound, brom ester, and zinc were, in the main, carried out as described in our first paper. In a few cases we met with unexpected difficulties, owing to the peculiar inactivity of the brom ester. Thus, when we used a fresh supply of methyl bromacetate we found it quite impossible to start a reaction either with saturated or unsaturated ketones. The preparation contained no hydrobromic acid, was free from water and alcohol, had a constant boiling point, and gave correct results on analysis—seemed in fact, to be an unusually pure substance. We met with the same difficulty while using brommalonic ester that we had prepared ourselves. In these cases it was necessary to use a catalyst. We found that none of the methods devised for getting more active magnesium in the preparation of Grignard reagents could be used with zinc; but that it is easy to start the reaction by adding a very small quantity of some organic copper compound that is soluble in benzene. We used copper acetacetic ester, and we have found that even when it is possible to start a slow reaction without it, better yields are sometimes obtained by adding a small quantity of copper derivative than by protracted boiling. With nitro compounds, saturated or unsaturated, the reaction fails completely even in the presence of a catalyst.

Our treatment of the product of the reaction depended upon the object of the experiment. When the reaction was used for the purpose of determining the relative amounts of 1,2- and 1,4-addition, the benzene solution was poured directly into sodium carbonate and distilled with steam as long as anything went into solution. In case the object was to isolate the substances formed, the benzene solution was usually poured into iced acid, the benzene layer washed thoroughly and dried, and the benzene evaporated in a draught. The residue generally contained a number of substances because in most cases spatial as well as structural isomers were formed. The isolation of all of these substances is frequently difficult even though each one crystallizes well when pure. Great care must be taken to remove all free acid before concentrating the solution, because in the presence of acid the solid unsaturated hydroxy esters rapidly pass into viscous liquids that interfere with the crystallization of everything present.

### *Experiments with Bromacetic Ester*

We repeated the reaction between bromacetic ester and benzalacetophenone described in the first paper, but took special precautions to detect any 1,4-addition product that might be formed. Thus, in one experiment in which more than 200 grams of benzalacetophenone were used, we separated the solid hydroxy ester as far as possible by crystallization, and then oxidized the accumulated residues with potassium permanganate at a temperatnre that was never allowed to rise above —10°. Parallel tests showed that in acetone solution the hydroxy ester is oxidized fairly rapidly, while methyl benzoylphenylbutyrate—the ketonic ester that would be formed by 1,4-addition—is not attacked at this temperature. We examined the oxidation products with care, but could not find a trace either of the ketonic ester or of the corresponding acid. We then repeated the experiment, but heated the residue with sodium carbonate in a current of steam. This also gave a negative result. Finally we destroyed the hydroxy ester by heating. Methyl hydroxyphenylbenzalbutyrate decomposes into benzalacetophenone and methyl acetate below 180°; the isomeric ketonic ester does not change below 260°. We heated to 200° until methyl acetate ceased to distil, and found the residue free from ketonic ester. From these results we are compelled to conclude that no 1,4-addition takes place with methyl bromacetate.

*γ-Benzal-β-hydroxy-β-phenylbutyric Acid*,



$$C_6H_5.CH : CH.\underset{\substack{| \\ CH_2.COOH}}{C}(OH)C_6H_5.$$

—When the methyl ester obtained in the experiments described above is treated with aqueous or alcoholic potassium hydroxide it is rapidly decomposed into benzalacetophenone and potassium acetate. By heating with sodium carbonate in a current of steam it is possible, however, to hydrolyze it with a yield of more than 70 per cent. of the corresponding acid. This was purified by crystallization from ether and ligroin. It is readily soluble in alcohol and ether, very sparingly in ligroin. From ether it separates in colorless needles that melt with decomposition at about 147°, when heated rapidly in a capillary tube. When heated slowly the acid loses both carbon dioxide and water far below the melting point.

Analysis:

0.1316 gram substance gave 0.3652 gram $CO_2$ and 0.0683 gram $H_2O$.

| | Calculated for $C_{17}H_{16}O_3$ | Found |
|---|---|---|
| C | 76.1 | 75.9 |
| H | 5.9 | 5.8 |

*β-Phenylcinnamylidenacetic Acid*, $C_6H_5.CH : CH.C(C_6H_5) : CH.COOH$.—While working with methyl bromacetate and benzalacetophenone we occasionally obtained a considerable quantity of an exceedingly viscous oil instead of the crystalline hydroxy ester. We found that the oil is formed whenever the ester is warmed in the presence of a small quantity of hydrochloric acid. The oil was hydrolyzed by boiling with alcoholic potassium hydroxide. It yielded a solid acid that crystallized from ether in fine, very pale yellow needles, melting at 145°–146°.

Analysis:

0.1413 gram substance gave 0.4235 gram $CO_2$ and 0.0770 gram $H_2O$.

| | Calculated for $C_{17}H_{14}O_2$ | Found |
|---|---|---|
| C | 81.6 | 81.7 |
| H | 5.6 | 6.1 |

### *Experiments with Brompropionic Ester*

The reaction with ethyl α-brompropionate was easily started and it proceeded rapidly, all of the zinc disappearing after boiling for less than an hour. The resulting benzene solution was poured into a saturated solution of sodium carbonate and heated in a rapid current of steam. At intervals of 5 hours the mixture was cooled, extracted with ether, the aqueous layer removed, and the ethereal solution heated with sodium carbonate as before. This was repeated as long as organic acid was obtained by acidifying the carbonate solution. The crude acid obtained by acidifying all the solutions in this way represented 46 per cent. of the benzalacetophenone used in the experiment. The last fractions melted between 130° and 140° and gave off a small quantity of gas when heated above 150°. They therefore probably contained a small quantity of hydroxy acid, but the only substance that could be isolated in pure form was a ketonic acid melting at 149°.

The separation of the products of the reaction proved difficult, the best results being obtained as follows: The benzene solution was diluted with ether and the mixture shaken with dilute hydrochloric acid. The ethereal layer was then separated and poured into a solution of sodium carbonate and heated in a current of steam for an hour. The solvents and excess of brom ester were carried off by the steam and any lactones formed in the reaction went into solution as sodium salts of ketonic acids, while the esters in the main remained unchanged, because they are very slowly saponified by sodium carbonate. The mixture was shaken with ether, the aqueous layer acidified, and the ethereal layer evaporated. The aqueous layer yielded two acids (4.5 grams from 42 grams of benzalacetophenone) that were separated by recrystallization from ether and ligroin. When pure, these melted at 149° (2 grams) and 107°.

The ethereal solution deposited a mixture of esters that was separated by repeated crystallization from methyl alcohol. The principal product was an ester melting at 107°, the remainder consisting mainly of an isomeric ester melting at 81°.

*Ethyl γ-Benzal-β-phenyl-β-hydroxy-α-methylbutyrate*, $C_6H_5.CH:CH.C(OH)(C_6H_5)CH(CH_3)COOC_2H_5$, the ester melting at 107°, is readily soluble in alcohol and ether, insoluble in ligroin. It crystallizes in fine needles.

Analysis:

0.1518 gram substance gave 0.4302 gram $CO_2$ and 0.0996 gram $H_2O$.

| | Calculated for $C_{20}H_{22}O_3$ | Found |
|---|---|---|
| C | 77.4 | 77.3 |
| H | 7.1 | 7.3 |

The ester is oxidized slowly by a cold solution of potassium permanganate in acetone, decomposes into benzalacetophenone and ethyl butyrate when heated above the melting point, gives benzalacetophenone and potassium propionate when warmed with alcoholic potassium hydroxide, and instantly decolorizes a solution of bromine at the ordinary temperature. It is therefore an unsaturated hydroxy ester as formulated.

The *ester melting at 81°* was obtained only in small quantities. It separates slowly from alcohol in large transparent prisms readily soluble in all common organic solvents except ligroin.

Analysis:

0.1584 gram substance gave 0.4527 gram $CO_2$ and 0.1012 gram $H_2O$.

| | Calculated for $C_{20}H_{22}O_3$ | Found |
|---|---|---|
| C | 77.4 | 78.0 |
| H | 7.1 | 7.2 |

The analysis shows that the ester is isomeric with the ester melting at 107°, and its properties indicate that it is another hydroxy ester. It reduces permanganate, decolorizes bromine, and is decomposed into benzalacetophenone and potassium propionate by treatment with alcoholic potassium hydroxide. It is therefore a stereoisomer of the ester melting at 107°.

*γ-Benzal-β-phenyl-α-methylbutyric Acid*, $C_6H_5.CO.CH_2.CH(C_6H_5)CH(CH_3)COOH$.—As stated above, the acid obtained in largest quantity by heating the product of the reaction with sodium carbonate melts at 149°. This acid separates from a mixture of ether and ligroin in fine feathery needles.

Analysis:

0.1557 gram substance gave 0.4383 gram $CO_2$ and 0.0918 gram $H_2O$.

| | Calculated for $C_{18}H_{18}O_3$ | Found |
|---|---|---|
| C | 76.6 | 76.7 |
| H | 6.4 | 6.6 |

The acid can be heated far above its melting point without causing decomposition. It does not combine with bromine and is not decomposed by boiling with alcoholic potassium hydroxide. It is therefore not an unsaturated hydroxy acid formed by addition to carbonyl, but a saturated ketonic acid formed by 1,4-addition. Like other ketonic acids of this character, it slowly reduces permanganate at the ordinary temperature.

The *acid melting at 105°* is likewise a ketonic acid because it has the same chemical properties as the acid melting at 149°. The analysis shows that it is isomeric with that acid; it is therefore a stereoisomer, possible because the ketonic acids have 2 dissimilar asymmetric carbon atoms. The acid crystallizes in very fine needles readily soluble in alcohol and ether, sparingly in ligroin.

Analysis:

0.1345 gram substance gave 0.3800 gram $CO_2$ and 0.0777 gram $H_2O$.

| | Calculated for $C_{18}H_{18}O_3$ | Found |
|---|---|---|
| C | 76.6 | 77.0 |
| H | 6.4 | 6.5 |

*Methyl γ-Benzoyl-β-phenyl-α-methylbutyrate*, $C_6H_5.CO.CH_2.CH(C_6H_5)CH(CH_3)COOCH_3$.—This ester was prepared by saturating the solution of the ester melting at 149° in methyl alcohol with hydrogen chloride, and purifying the product by recrystallization from methyl alcohol. It crystallizes in fine needles melting at 68°.

Analysis:

0.1309 gram substance gave 0.3720 gram $CO_2$ and 0.0813 gram $H_2O$.

| | Calculated for $C_{19}H_{20}O_3$ | Found |
|---|---|---|
| C | 77.0 | 77.5 |
| H | 6.7 | 6.9 |

The corresponding *ethyl ester* was prepared in the same way. It crystallizes in needles melting at 41°.

Analysis:

0.1358 gram substance gave 0.3849 gram $CO_2$ and 0.0858 gram $H_2O$.

| | Calculated for $C_{20}H_{22}O_3$ | Found |
|---|---|---|
| C | 77.4 | 77.3 |
| H | 7.1 | 7.1 |

The low melting point of this ester explains why it cannot be isolated from the product of the reaction between benzalacetophenone, α-brompropionic ester and zinc, even though it composes a large part of this product. As shown by the above results, this reaction gives at least 5, and possibly 6, substances: two stereoisomeric hydroxy esters, one or two ketonic esters, and one or two lactones. The presence of lactones is inferred from the relatively large quantity of acid obtained by boiling the product with a solution of sodium carbonate for a short time.

### *Experiments with Brombutyric Ester*

The reaction with methyl α-brombutyrate goes so slowly that we found it advisable to use a small quantity of copper-acetacetic ester as catalyst. For the purpose of determining the relative amounts of 1,2- and 1,4-addition, the benzene solution was poured into sodium carbonate and heated as described under the experiments with brompropionic ester. The quantity of crude ketonic acid obtained by this procedure represented 50 per cent. of the benzalacetophenone used. The acid was entirely free from hydroxy acid. It was purified by recrystallization from alcohol.

*γ-Benzoyl-β-phenyl-α-ethylbutyric acid,*

$C_6H_5.CO.CH_2.CH(C_6H_5)CH(C_2H_5)COOH$,

crystallizes in needles melting at 181°.

Analysis:

0.1355 gram substance gave 0.3809 gram $CO_2$ and 0.0825 gram $H_2O$.

| | Calculated for $C_{19}H_{20}O_3$ | Found |
|---|---|---|
| C | 77.0 | 76.8 |
| H | 6.7 | 6.8 |

The acid does not combine with bromine, and does not decompose when heated above its melting point, but, like other ketonic acids previously described, slowly reduces permanganate at the ordinary temperature.

The *methyl ester* was made by saturating a solution of the acid in methyl alcohol with hydrogen chloride. It separates from methyl alcohol in fine needles melting at 95°.

Analysis:

0.1425 gram substance gave 0.4045 gram $CO_2$ and 0.0909 gram $H_2O$.

| | Calculated for $C_{20}H_{22}O_3$ | Found |
|---|---|---|
| C | 77.4 | 77.3 |
| H | 7.1 | 7.2 |

*Methyl γ-Benzal-β-phenyl-β-hydroxy-α-ethylbutyrate,* $C_6H_5.CH : CH.C(C_6H_5)(OH).CH(C_2H_5)COOCH_3$.—The hydroxy ester is easily obtained by decomposing the zinc compounds in the usual way. It crystallizes in needles melting at 117°.

Analysis:

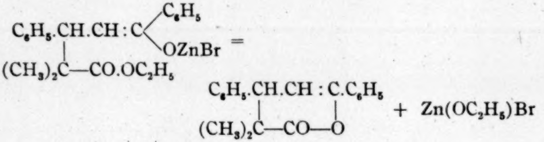
0.1324 gram substance gave 0.3757 gram $CO_2$ and 0.0836 gram $H_2O$.

| | Calculated for $C_{20}H_{22}O_3$ | Found |
|---|---|---|
| C | 77.4 | 77.4 |
| H | 7.1 | 7.2 |

The ester combines with bromine, reduces permanagnate, and above its melting point decomposes cleanly into benzalacetophenone and methyl butyrate.

### *Experiments with Bromisobutyric Ester*

In order to get a complete reaction between benzalacetophenone, ethyl bromisobutyrate, and zinc, it is necessary to use an excess of at least ten per cent. both of ester and zinc because a part of these substances is lost in secondary processes. The final result of the reaction in this case depends, to a considerable extent, upon the concentration and the amount of heating. In concentrated solutions, in which the reaction proceeds rapidly after it is once started, the principal product is an unsaturated lactone. In dilute solution, in which the substances react more slowly, the principal product is, usually, a ketonic ester; but if the dilute solution is boiled for a long time the ketonic ester steadily disappears and a relatively larger amount of lactone is obtained. The lactone is, therefore, formed at the expense of the zinc derivative of the ester:



$$\begin{array}{l} C_6H_5.CH.CH:C\!\begin{array}{l}\diagup C_6H_5\\ \diagdown OZnBr\end{array} \\ \qquad\;\,| \\ (CH_3)_2C\text{—}CO.OC_2H_5 \end{array} = \begin{array}{l} C_6H_5.CH.CH:C.C_6H_5 \\ \qquad\;\,|\qquad\qquad\;| \\ (CH_3)_2C\text{—}CO\text{—}O\end{array} + Zn(OC_2H_5)Br$$

The most convenient way of getting pure products from the reaction is as follows: The mixture is poured into acid and washed as usual. The benzene layer is then poured into water and distilled in a rapid current of steam for an hour. This removes the benzene, any unchanged materials, and most of the secondary products. The residue is dissolved in ether and this solution extracted with sodium carbonate to save a variable quantity of acid that is formed from the lactone during distillation. The ethereal solution, on evaporation, deposits a mixture of lactone and acid contaminated with a small quantity of yellow oil. The solid is washed with methyl alcohol that has been cooled in a freezing mixture and then recrystallized from the same solvent. The lactone separates first and, from concentrated solution, almost completely, while the ketonic ester remains in solution until most of the solvent has evaporated if crystallization is not started by the addition of a small quantity of solid. The lactone is very sparingly soluble in ligroin, moderately in ether and cold alcohol, readily in acetone. It crystallizes in long colorless needles melting at 97°.

Analysis:

0.1744 gram substance gave 0.5228 gram $CO_2$ and 0.1008 gram $H_2O$.

| | Calculated for $C_{19}H_{18}O_2$ | Found |
|---|---|---|
| C | 82.0 | 81.7 |
| H | 6.5 | 6.4 |

The substance reduces a solution of potassium permanganate in acetone in the cold and combines with bromine below 0°. The lactone ring is slowly opened by boiling with water, more rapidly by boiling with sodium carbonate, immediately by solution in alcoholic potassium hydroxide.

*γ-Benzoyl-β-phenyl-α,α-dimethylbutyric Acid,* $C_6H_5.CO.CH_2.CH(C_6H_5)C(CH_3)_2COOH$, the acid obtained from the lactone, was purified by crystallization from methyl alcohol. It separates in fine white needles melting at 159°–160°.

Analysis:

0.1142 gram substance gave 0.3228 gram $CO_2$ and 0.0678 gram $H_2O$.

| | Calculated for $C_{19}H_{20}O_3$ | Found |
|---|---|---|
| C | 77.0 | 77.1 |
| H | 6.8 | 6.6 |

The acid is sparingly soluble in ether and chloroform, readily in alcohol and acetone. Its solution in sodium carbonate does not reduce potassium permanganate in the cold, but the color rapidly disappears on warming. The acid does not react with bromine at the ordinary temperature, but by adding bromine to a hot solution of the acid in chloroform or carbon tetrachloride it is easy to replace one of the hydrogen atoms in combination with the carbon atom that adjoins the carbonyl group.

*Ethyl γ-Benzoyl-β-phenyl-α,α-dimethylbutyrate,*
$C_6H_5.CO.CH_2CH(C_6H_5)C(CH_3)_2COOC_2H_5$.—The ester was sep-

arated from the mother liquor after removing the lactone. It was also made from the acid by saturating its solution in absolute alcohol with hydrogen chloride, and from the lactone by the same procedure. It is readily soluble in ether and alcohol, sparingly in ligroin. It separates from methyl alcohol in needles melting at 83°.

Analysis:

0.1512 gram substance gave 0.4317 gram $CO_2$ and 0.1003 gram $H_2O$.

| | Calculated for $C_{21}H_{24}O_3$ | Found |
|---|---|---|
| C | 77.8 | 77.8 |
| H | 7.4 | 7.4 |

The *methyl ester*, made and purified like the ethyl ester, crystallizes in needles melting at 92°. As it is less soluble and crystallizes much more readily than the ethyl ester it is a much more convenient substance to work with.

Analysis:

0.1211 gram substance gave 0.3449 gram $CO_2$ and 0.0790 gram $H_2O$.

| | Calculated for $C_{20}H_{22}O_3$ | Found |
|---|---|---|
| C | 77.4 | 77.6 |
| H | 7.1 | 7.2 |

*γ-Brom-γ-benzoyl-β-phenyl-α,α-dimethylbutyric acid,*

$C_6H_5.CO.CHBrCH(C_6H_5)C(CH_3)_2COOH$,

the acid obtained by adding the calculated amount of bromine to a hot solution of the ketonic acid in chloroform or carbon tetrachloride, is so unstable that we found it exceedingly difficult to get a pure product. By dissolving it in acetone at the ordinary temperature, adding an equal volume of carbon tetrachloride to this solution, and then cooling in a freezing mixture, we finally obtained long, colorless needles that gave consistent analytical results. The acid begins to decompose slowly below the melting point, which is consequently inconstant; but on rapid heating in a capillary tube, the substance seems to melt and decompose fairly sharply at 186°.

Analysis:

0.1610 gram substance gave 0.3607 gram $CO_2$ and 0.0765 gram $H_2O$.

| | Calculated for $C_{19}H_{19}O_3Br$ | Found |
|---|---|---|
| C | 60.9 | 61.1 |
| H | 5.1 | 5.3 |

The esters of the acid were easily made by adding bromine to a solution of the corresponding ketonic esters in carbon tetrachloride. It is necessary to start the reaction by heating, but after that the bromine disappears as fast as it is added, until the solution contains one molecule of bromine per molecule of ester. The solution in carbon tetrachloride, on evaporation, deposits the esters in solid form, and they are readily purified by recrystallization from methyl alcohol.

The *methyl ester* crystallizes in large prisms, moderately soluble in ether and cold alcohol, readily soluble in boiling alcohol. The melting point is 125°.

Analysis:

0.1457 gram substance gave 0.3286 gram $CO_2$ and 0.0720 gram $H_2O$.

| | Calculated for $C_{20}H_{21}O_3Br$ | Found |
|---|---|---|
| C | 61.9 | 61.6 |
| H | 5.4 | 5.5 |

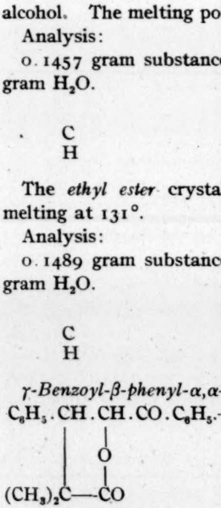
The *ethyl ester* crystallizes in fine needles or thin plates melting at 131°.

Analysis:

0.1489 gram substance gave 0.3431 gram $CO_2$ and 0.0802 gram $H_2O$.

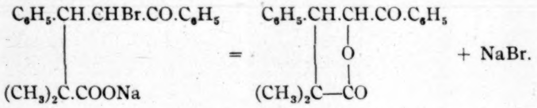
| | Calculated for $C_{21}H_{23}O_3Br$ | Found |
|---|---|---|
| C | 62.5 | 62.8 |
| H | 5.7 | 6.0 |

*γ-Benzoyl-β-phenyl-α,α-dimethylbutyrolactone,*



$$\begin{array}{l} C_6H_5.CH.CH.CO.C_6H_5 \\ \qquad\ |\qquad | \\ \qquad\ |\qquad O \\ \qquad\ |\qquad | \\ (CH_3)_2C\text{—}CO \end{array}$$

—Brombenzoylphenyldimethylbutyric acid, when finely powdered, dissolves readily in dilute sodium carbonate, but the solution stays clear only a very short time. A faint milkiness appears in a few minutes and in the course of an hour the liquid becomes filled with a network of fine needles that represent practically all of the acid dissolved. The solid consists of two stereoisomeric lactones formed as represented by the equation



$$\begin{array}{l} C_6H_5.CH.CHBr.CO.C_6H_5 \\ \qquad | \\ \qquad | \\ (CH_3)_2C.COONa \end{array} = \begin{array}{l} C_6H_5.CH.CH.CO.C_6H_5 \\ \qquad |\quad | \\ \qquad |\quad O \\ \qquad |\quad | \\ (CH_3)_2C—CO \end{array} + NaBr.$$

The lactones were separated as follows: The solid was filtered, washed thoroughly with boiling water, dried, and extracted with boiling methyl alcohol. This extracted, mainly, the lower-melting lactone, which had a constant melting point of 113° after a few recrystallizations from the same solvent. The residue, left after extraction with methyl alcohol, was recrystallized from acetone until the melting point remained constant at 173°. Both lactones crystallize in colorless needles.

Analyses:

I. 0.1313 gram substance (low melting) gave 0.3726 gram $CO_2$ and 0.0741 gram $H_2O$.

II. 0.1442 gram substance (high melting) gave 0.4090 gram $CO_2$ and 0.0815 gram $H_2O$.

|  | Calculated for $C_{19}H_{18}O_3$ | Found I | Found II |
|---|---|---|---|
| C | 77.6 | 77.4 | 77.4 |
| H | 6.1 | 6.3 | 6.3 |

The lactones are not affected by hot sodium carbonate, but they dissolve readily in cold alcoholic potassium hydroxide. If the pale yellow solutions obtained in this way are allowed to stand for some time they give only complex products when acidified; but if they are acidified immediately they give the corresponding hydroxy acid. The same two acids are formed from each lactone: a small quantity of a high-melting, sparingly soluble acid that loses water so readily that it was impossible to get it free from the high-melting lactone, and a low-melting acid that was purified by recrystallization from ether. It separates in needles that lose water below the melting point, but on rapid heating melt fairly sharply at 126°. When heated to 120° for several hours the acid passes completely into the low-melting lactone. The results of an analysis show that this acid is *γ-benzoyl-γ-hydroxy-β-phenyl-α,α-dimethylbutyric acid*,

$$C_6H_5.CO.CHOH.CH(C_6H_5)C(CH_3)_2COOH.$$

Analysis:

0.1410 gram substance gave 0.3793 gram $CO_2$ and 0.0815 gram $H_2O$.

| | Calculated for $C_{19}H_{20}O_4$ | Found |
|---|---|---|
| C | 73.1 | 73.4 |
| H | 6.3 | 6.4 |

### *Experiments with Brommalonic Ester*

*Methyl Brommalonate*, $BrCH(CO_2CH_3)_2$.—As the ethyl ester of brommalonic acid gave only oily products we prepared the methyl ester by gradually adding the calculated quantity of bromine to methyl malonate and fractionating the product under diminished pressure. The reaction starts slowly, but, once started, proceeds rapidly at the ordinary temperature. The yield is unsatisfactory. The best result—about 70 per cent. of the calculated amount of pure product—was obtained when the crude product was heated under diminished pressure and finally distilled without preliminary washing. The ester is a colorless, mobile liquid boiling at 145° (22 mm.).

Analysis:

0.1582 gram substance gave 0.1410 gram AgBr.

| | Calculated for $C_5H_7O_4Br$ | Found |
|---|---|---|
| Br | 37.92 | 38.03 |

*Methyl γ-Benzoyl-β-phenylethylmalonate*, $C_6H_5.CO.CH_2.CH(C_6H_5)CH(CO_2CH_3)_2$.—The product obtained from methyl brommalonate, benzalacetophenone and zinc partially solidified when the benzene solution was evaporated. The solid was easily purified by a few recrystallizations from methyl alcohol. It is sparingly soluble in ligroin, moderately in ether and methyl alcohol, readily in alcohol, chloroform, and acetone. From methyl alcohol it separates in large, colorless needles melting at 107°.

Analysis:

0.1163 gram substance gave 0.3017 gram $CO_2$ and 0.0652 gram $H_2O$.

| | Calculated for $C_{20}H_{20}O_5$ | Found |
|---|---|---|
| C | 70.6 | 70.8 |
| H | 5.9 | 6.23 |

On hydrolysis with alcoholic potassium hydroxide the ester gave a dibasic acid that readily lost carbon dioxide when heated to 170°. The resulting monobasic acid, after recrystallization from ether, melted at 156°. It was identified as γ-benzoyl-β-phenylbutyric acid by comparison with a specimen on hand. The solid is, therefore, the methyl ester of the dibasic acid obtained by Vorländer[1] by condensing benzalacetophenone and sodium malonic ester and hydrolyzing the product with alcoholic potassium hydroxide. Only about one-third of the product was obtained in solid form, the remainder consisting of a viscous liquid that decomposed when distilled under diminished pressure. This liquid is apparently a lactonic ester formed from the zinc compound in the usual way. When boiled with sodium carbonate it slowly goes into solution and is precipitated as an oily acid when the solution is acidified. With alcoholic potassium hydroxide it gives the same acid that is obtained from the solid ester.

Very little, if any, 1,2-addition product is formed in the reaction between benzalacetophenone, brommalonic ester and zinc. We have prepared the unsaturated hydroxy ester that would be formed by 1,2-addition in another way, and know that it is very rapidly decomposed into benzalacetophenone and malonate by boiling with sodium carbonate. As the entire product from the zinc compound gave only a very small quantity of benzalacetophenone when boiled with sodium carbonate the amount of hydroxy ester present is certainly small. Moreover, since the ketonic ester formed by 1,4-addition is slowly decomposed by the treatment, it is quite possible that the small quantity of unsaturated ketone obtained was derived from this source.

---

[1] Ann. Chem. (Liebig), **294**, 332.

# ANHYDROUS FORMIC ACID[1]

BY JAMES B. GARNER, BLAIR SAXTON AND H. O. PARKER

[PRELIMINARY PAPER]

For some time past several students, working in the laboratory here, have been studying the absorption spectra of solutions of the various indicators. In connection with this work results were obtained which necessitated a study of solutions of these substances in some other solvent than water. Formic acid was selected for the study on account of the fact that all its physical constants were supposed to be more nearly like those of water than those of any other ordinary solvents.

The examination of the text-books, books of reference, and the literature, disclosed the following: (1) That there are no well defined, accurately described methods of preparation of anhydrous formic acid. (2) That there is very little agreement in books or among authors as to the values of the various physical constants.

## *Methods of Preparation which have been Used*

Fractional crystallization was the method used by Petersson,[2] Bannow,[3] Hartwig,[4] Sapojnikoff,[5] Tessarin,[6] and other investigators.

---

[1] This paper was read before the Section of Physical and Inorganic Chemistry of the Americn Chemical Society, at Indianapolis, Indiana.

[2] J. prakt. Chem., **24**, 296 (1881).

[3] Ber. d. chem. Ges., **9**, 4.

[4] J. Chem. Soc., **60**, 1308.

[5] *Ibid.*, **66**, 66.

[6] Z. physik. Chem., **19**, 251.

Vol. 46
1911

Kahlbaum,[1] Schiff,[2] and the Chemische Fabrik, Grünau,[3] attempted to prepare the pure acid by fractional distillation under diminished pressure with sulphuric and metaphosphoric acids and acid salts as dehydrating reagents. The maximum concentration obtained by any of these investigators was 97 to 98 per cent.

Richardson and Allaire[4] prepared what they regarded as the pure anhydrous acid by repeated distillation over dry lead formate.

### *Physical Constants which are Given*

The following selection will clearly show the disagreements which exist as to the value of the various physical constants:

(1) In reference to melting point:

| Melting Point | Investigator | Reference |
|---|---|---|
| 8°.0 | Berthollet | |
| 4°.0 | Bannow | Ber. d. chem. Ges., **9,** 4 |
| 8°.43 | Petersson and Ekstrand | *Ibid.*, **13,** 1880 |
| Note: No description of method of preparation given. | | |
| 7°.45 | Petersson | J. prakt. Chem., **24,** 296 |
| 8°.39 | Sapojnikoff | J. Chem. Soc., **66,** 66 |
| 8°.00 | Miss Homfray | *Ibid.*, **87,** 1436 |
| 5°.65, 6°.5, 6°.6, 6°.9, and 7°.1 | Tessarin | Z.physik.Chem., **19,** 251 |

(2) The following data with reference to specific gravity measurements at 20° C. clearly illustrate the situation:

| Sp. Gr. at 20° | Investigator | Reference |
|---|---|---|
| 1.219 | J. Traube | Ber. d. chem. Ges., **19,** 884 |
| 1.2213 | Richardson and Allaire | This Journal, **19,** 149 |
| 1.2205 | Miss Homfray | J. Chem. Soc., **1905,** 1436 |
| 1.223 | Tessarin | Z. physik. Chem., **19,** 251 |
| 1.235 | Liebig | Smithsonian Tables |

(3) The following table shows the uncertainty which exists as to the true boiling point of anhydrous formic acid:

---

[1] Ber. d. chem. Ges., **16,** 2480.

[2] *Ibid.*, **19,** 561.

[3] J. Chem. Soc., **1908,** 598.

[4] This Journal, **19,** 149 (1897).

| Temp. | Pressure | Investigator | Reference |
|---|---|---|---|
| 100° | 760 | Schiff | Smithsonian Tables |
| 100° | 760 | Favre and Silbermann | |
| 100° | 760 | Landolt | |
| 100° | 760 | Zander | |
| 100° | 760 | Roscoe | |
| 101°.0 | 760 | Tessarin | Z. physik. Chem., **19**, 251 |
| 100°.6 | 760 | Kopp | |
| 100°.6 | 760 | Kahlbaum | Ber. d. chem. Ges., **16**, 2480 |
| 100°.3 | 763.5 | Schiff | *Ibid.*, **19**, 561 |
| 98°.5 | 748 | Liebig | |
| 99°.4 | 748 | Landolt | |
| 100°.5 | 749 | Petersson and Ekstrand | Ber. d. chem. Ges., **13**, 1880 |

Our first task therefore was the preparation of the pure substance and our second task that of the accurate determination of the physical constants.

### *Method of Preparation*

When method of Richardson and Allaire, namely, that of repeated distillation from dry lead formate, was used the acid obtained had the melting point 7°.91. The methods of Kalhbaum, Schiff, and the Chemische Fabrik, Grünau, were also used. It was found that phosphorus pentoxide and sulphuric acid act destructively. Formic acid decomposes violently into carbon monoxide and water under all the varying pressures. The yield is very poor. The acid thus obtained has a melting point of 8°.

The laborious method of fractional recrystallization gave us an acid melting at 8°.34. Distillation under diminished pressure over anhydrous nickel sulphate yielded an acid melting at 8°.21. The acid obtained by distillation under diminished pressure over anhydrous sodium sulphate melted at 8°.27. Distillation under diminished pressure, 120 mm. at 50°, over anhydrous copper sulphate gave us an acid melting constantly at 8°.35. This last method of preparation we regard as the most satisfactory and efficient. Beginning with the acid having a melting point of 7°.26, the first distillation results in an acid melting at 8°, the second in one having a melting point of 8°.21, and the third distillation yields an acid melting at 8°.31, while the fourth, fifth, and sixth distillations all give an acid which melts at 8°.35.

The analyses of the acid melting at 8°.35 show it to be the pure anhydrous acid.

I. 0.4276 gram substance gave 0.4103 gram $CO_2$ and 0.1704 gram $H_2O$.

II. 0.9512 gram substance gave 0.9048 gram $CO_2$ and 0.3957 gram $H_2O$.

| | Calculated | Found I | Found II |
|---|---|---|---|
| C | 26.09 | 26.18 | 25.95 |
| H | 4.38 | 4.46 | 4.65 |

*Physical Constants*

(*a*) The following values of the specific gravity were obtained:

| | I | II |
|---|---|---|
| 10° | 1.2322 | 1.2322 |
| 15° | 1.2360 | 1.2260 |
| 20° | 1.2200 | 1.2199 |
| 25° | 1.2139 | 1.2139 |
| 30° | 1.2078 | 1.2079 |
| 35° | 1.2019 | 1.2019 |
| 40° | 1.1957 | 1.1956 |

(*b*) Viscosity measurements resulted as follows:

| | C. G. S. units | Gartenmeister's values (Smithsonian tables) |
|---|---|---|
| 10° | 0.0226 | 0.0231 |
| 15° | 0.02002 | |
| 20° | 0.01793 | 0.0184 |
| 25° | 0.01625 | |
| 30° | 0.01474 | 0.0149 |
| 35° | 0.01343 | |
| 40° | 0.01218 | 0.0125 |

(*c*) Boiling-point determinations were:

| Temp. | Pressure mm. |
|---|---|
| 50° | 120 |
| 99°.7 | 741 |

(*d*) Surface tension, refractive index, specific heat, and specific conductivity measurements are being made.

(*e*) Experiments are in progress which have for their purposes: (1) The determination of the conditions—time, temperature, friction, and presence of solid state—which influence the spontaneous crystallization of supercooled anhydrous formic acid. (2) The determination of the range of the metastable state. We have found that formic acid may be readily cooled to 14°.35 below its melting point in ordinary glass vessels. Even with vigorous stirring, it supercools to 5°.8, or 2°.55 below the melting point.

It is the intention of the authors to continue the work with anhydrous formic acid to determine the following:

(1) The variation of solubility of electrolytes with the temperature.

(2) The relationship between dissociation constant and heat of dissociation.

(3) The relationship between molecular conductivities of salts and increasing dilution.

(4) The relationship between dielectric constant and dissociating power.

(5) The relationship between association factor and conductivity; and

(6) The relationship between viscosity and conductivity.

Peck Chemical Laboratory
Wabash College
Crawfordsville, Ind.

# THE CONDUCTIVITIES, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND DISSOCIATION OF CERTAIN ELECTROLYTES

By H. H. Hosford and Harry C. Jones

## HISTORICAL REVIEW

Volta, at the end of the eighteenth century, distinguished two classes of conductors of the then recently discovered galvanism. The first class comprised those substances, such as metals, which conduct without chemical change; while conductors of the second class were decomposed by the passage of the current. A few years later, by electrolyzing conductors of the second class, Davy isolated the previously unknown metals of the alkalies and the alkaline earths. Faraday,[1] in 1832, published his laws showing the relation between the amount of electricity passed through the electrolyte and the amount of the electrolyte decomposed.

Measurements of the resistance of solutions of electrolytes were soon made by many investigators. Of these early researches those of Hankel,[2] Becquerel,[3] Horsford,[4] Wiedeman,[5] Becker,[6] and Beetz[7] may be especially noted. Brief discussions of these and other investigations can be found in Wiedemann's book.[8]

The earlier methods were very imperfect. The continuous current was used, causing polarization of the electrodes, except in some special cases, as when the metal of the salt was used for the electrodes. The standard method now used practically eliminates polarization by using the alternating current. This method was first developed and used by Kohlrausch and his coworkers in a series of researches[9] that were far more comprehensive than any preceding investigations.

The dissociation theory of Arrhenius[10] imparted new life to conductivity measurements of electrolytes as affording a basis for the accurate determination of the degree of ionization.

Following Kohlrausch, many investigations in this field have been carried out, but in most cases with some special object in view which has limited the scope of the work. The researches were concerned with a few substances only, or were confined to a narrow range of temperature and concentration.

[1] Exp. Researches, III, Ser. No. **373** (1832).

[2] Pogg. Ann., **69,** 255 (1846).

[3] Ann. chim. phys., [3] **17,** 365 (1864).

[4] Pogg. Ann., **70,** 238 (1847).

[5] *Ibid.*, **99,** 225 (1856).

[6] Ann. Chem. (Liebig), **73,** 1 (1850); **75,** 94 (1851).

[7] Pogg. Ann., **117,** 1 (1862).

[8] G. Wiedemann: Die Lehre von der Elektricität, Band I (Braunschweig, 1882).

[9] For brief discussions and references to original publications see Wiedemann: *Loc. cit.*

[10] Z. physik. Chem., **1,** 631 (1881). Scientific Memoirs, Series IV, p. 47.

### PURPOSE OF THIS INVESTIGATION

It has seemed desirable to secure conductivity data relative to all the substances in more common use by the chemist, and under the conditions of temperature and dilution at which they are usually employed in chemical work. With this end in view, a systematic study of the electrical conductivities and allied relations of acids, bases and salts in aqueous as well as in nonaqueous solutions, and at various temperatures and concentrations, has been in progress in this laboratory for ten years. Six papers[1] dealing solely with aqueous solutions have been published and other investigations are in progress.

The work herein described was undertaken as a continuation of that already carried out on the general problem. It includes the determination of the electrical conductivities, temperature coefficients of conductivity and percentage dissociation of a number of inorganic salts at dilutions ranging from N/2 to N/4096. Some of the measurements were made over a range of temperature from 0° to 35°, and a part from 35° to 65°.

### PREPARATION OF MATERIAL

The salts used were the purest available. In nearly all cases Kahlbaum's chemicals were employed. These were recrystallized from one to five times, the final crystallizations in all cases being made from water of special purity or so-called "conductivity water." Any deviations from this general procedure are stated in connection with the experimental data under each salt.

The water used in making up the solutions was prepared by a modification of the method of Jones and Mackay,[2] i. e., by subjecting the distilled water of the laboratory to three additional distillations: first in the presence of potassium dichromate and sulphuric acid to oxidize organic matter and retain ammonia, and twice with barium hydroxide to absorb carbon dioxide. The conductivity of such water varies from

---

[1] Jones and Douglas: THIS JOURNAL, **26**, 428 (1901). Jones and West: *Ibid.*, **34**, 357 (1905). Jones and Jacobson: *Ibid.*, **40**, 355 (1908). Clover and Jones: *Ibid.*, **43**, 187 (1910). White and Jones: *Ibid.*, **44**, 159 (1910). West and Jones: *Ibid.*, **44**, 508 (1910).

[2] Z. physik. Chem., **14**, 317 (1894). THIS JOURNAL, **19**, 91 (1897).

$1.0$ to $1.5 \times 10^{-6}$. The correction of the molecular conductivity due to this cause is negligible in the greater concentrations, but was calculated and applied to the conductivity values obtained for the dilute solutions.

## APPARATUS AND METHOD

The Kohlrausch method was used in this investigation. In the work from 35° to 65° a slide-wire bridge of the usual type was employed, while measurements from 0° to 35° were made by means of an improved slide-wire bridge made by Leeds and Northrup, the wire being about five meters long. The bridges and resistance coils were standardized by Leeds and Northrup and also by means of resistances which had been corrected by the U. S. Bureau of Standards.

The conductivity cells were of the type used and described by Clover and Jones[1] and Jones and West.[2] The constants of these cells were determined at short intervals. In connection with the work from 0° to 35° the following method of determining the constants was employed. A 0.02 N solution of carefully purified potassium chloride was prepared, using water of special purity. The molecular conductivity of this solution at 25° was assumed to have Kohlrausch's value of 129.7, and this solution was used to determine the constants of the cells designed for concentrated solutions. A 0.002 N solution of potassium chloride was also prepared, and its molecular conductivity found by means of a cell whose constant had been determined as explained above. This 0.002 N solution was then used in finding the constants of the cells intended for the more dilute solutions.

In connection with the work from 0° to 35°, a slightly different plan was adopted. Solutions of potassium chloride of 0.02 N and 0.002 N concentration were prepared and used as described; but a fixed value of 136.5 at 25° was taken for the molecular conductivity of the 0.002 N solution. This value is based on repeated measurements made in this laboratory.

So far as possible the initial or mother solution of each salt was prepared by direct weighing of the properly purified substance. If this was impracticable a mother solution of convenient strength was made up and standardized by analysis. From the mother solution the various concentrations were prepared by dilution. In the case of the work from 0° to 35°, solutions were made up at 20° and were used without corrections at the various temperatures at which measurements were made, the correction being less than the known experimental error. When working from 35° to 65° solutions were prepared at 50°, and a factor was employed in the reduction of all measurements made at 35° and 65° to correct for the change in concentration due to change in volume. The correction factor for the molecular conductivity of solutions made at 50° and used at 35° is 0.994; for those made at 50° and used at 65° the value is 1.0076. The burettes and measuring flasks used in making up solutions were carefully calibrated for the temperature at which they were to be used.

---

[1] This Journal, **43,** 192 (1910).

[2] *Ibid.*, **44,** 510 (1910).

For the work at 0° an ice bath was employed in which the cells were supported so as to be immersed as deeply as possible in the crushed ice and water. A shallow vessel filled with ice and water covered the ice baths when in use. Connections were made through openings closed with perforated stoppers carrying the conducting wires. The baths for higher temperatures were properly sheathed with asbestos cement, and in the case of the 50° and 65° baths efficient covers were provided to retain the heat. Hot-air engines were used to stir the baths. It was found easy to keep the temperature of the baths constant to within 0°.02 or 0°.03 by hand regulation, and this method was adopted.

From two to four independent measurements of the conductivity were made for each concentration at each temperature. If there was not close agreement in the results, or if any abnormally large errors were suspected, the measurements were repeated. So far as possible our results were compared with those obtained by other workers. In most cases there is reasonable agreement. When wide discrepancies appeared our work was duplicated.

Concentrations are indicated under the heading *V*, or the number of liters which would contain one gram-molecular weight of the salt. Molecular conductivities are expressed in Siemens' units. The temperature coefficients and dissociation were calculated in the usual way. On account of hydrolysis or other causes, the maximum value of the molecular conductivity ($\mu_\infty$) was not found for certain salts at the greatest dilution worked with. In such cases the dissociation was not calculated.

### *Ammonium Aluminium Sulphate*, $NH_4Al(SO_4)_2.12H_2O$

The mother solution was standardized by determining aluminium as aluminium oxide.

*Table I.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 80.0 | 110.9 | 143.1 | 168.8 |
| 32 | 102.5 | 143.1 | 185.5 | 220.4 |
| 128 | 130.1 | 182.7 | 238.8 | 284.8 |
| 512 | 162.2 | 230.9 | 304.5 | 365.9 |
| 1024 | 181.0 | 257.5 | 342.4 | 415.1 |
| 2048 | 201.8 | 288.2 | 386.4 | 485.8 |
| 4096 | 224.1 | 322.8 | 437.6 | 540.3 |

*Table II.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 2.47 | 3.09 | 2.58 | 2.33 | 2.57 | 1.80 |
| 32 | 3.25 | 3.17 | 3.39 | 2.37 | 3.49 | 1.88 |
| 128 | 4.21 | 3.24 | 4.49 | 2.46 | 4.60 | 1.93 |
| 512 | 5.50 | 3.39 | 5.89 | 2.55 | 6.14 | 2.02 |
| 1024 | 6.12 | 3.38 | 6.79 | 2.64 | 7.27 | 2.12 |
| 2046 | 6.91 | 3.42 | 7.86 | 2.73 | 9.94 | 2.57 |
| 4096 | 7.90 | 3.53 | 8.38 | 2.60 | 10.27 | 2.35 |

### *Ammonium Chromium Sulphate (Violet Variety)*, $NH_4Cr(SO_4)_2.12H_2O$

The mother solution was standardized in the same manner as in the case of the potassium salt.

*Table III.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 77.5 | 106.4 | 137.3 | 162.7 |
| 16 | 88.9 | 123.2 | 159.5 | 188.3 |
| 32 | 100.8 | 140.3 | 182.2 | 216.0 |
| 128 | 129.5 | 183.0 | 240.2 | 285.9 |
| 512 | 165.5 | 238.0 | 321.0 | 385.9 |
| 1024 | 187.0 | 272.0 | 372.0 | 455.7 |
| 2048 | 211.9 | 310.7 | 428.5 | 530.0 |
| 4096 | 240.7 | 355.6 | 492.2 | 617.0 |

*Table IV.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 2.31 | 2.98 | 2.47 | 2.32 | 2.54 | 1.85 |
| 16 | 2.74 | 3.08 | 2.90 | 2.35 | 2.88 | 1.81 |
| 32 | 3.16 | 3.14 | 3.35 | 2.39 | 3.38 | 1.86 |
| 128 | 4.28 | 3.31 | 4.57 | 2.50 | 4.57 | 1.90 |
| 512 | 5.80 | 3.51 | 6.64 | 2.79 | 6.49 | 2.02 |
| 1024 | 6.80 | 3.64 | 8.00 | 2.94 | 8.37 | 2.25 |
| 2048 | 7.90 | 3.73 | 9.40 | 3.03 | 10.15 | 2.37 |
| 4096 | 9.19 | 3.82 | 10.93 | 3.07 | 12.48 | 2.54 |

### *Ammonium Chromium Sulphate (Green Variety)*

The mother solution was prepared by heating a portion of the mother solution of the violet variety to 70° for about seven hours in a stoppered bottle.

*Table V.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 103.6 | 133.2 | 162.9 | 185.3 |
| 16 | 119.7 | 155.4 | 190.6 | 219.3 |
| 32 | 136.4 | 178.2 | 220.8 | 255.1 |
| 128 | 172.3 | 228.4 | 288.1 | 336.4 |
| 512 | 202.6 | 274.4 | 355.7 | 423.2 |
| 1024 | 215.6 | 294.2 | 386.2 | 471.2 |
| 2048 | 222.0 | 313.5 | 414.0 | 518.4 |
| 4096 | 234.4 | 328.4 | 458.1 | 593.8 |

*Table VI.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 2.37 | 2.29 | 2.38 | 1.79 | 2.24 | 1.38 |
| 16 | 2.70 | 2.26 | 2.82 | 1.82 | 2.87 | 1.51 |
| 32 | 3.34 | 2.45 | 3.41 | 1.91 | 3.43 | 1.55 |
| 128 | 4.49 | 2.61 | 4.78 | 2.09 | 4.83 | 1.68 |
| 512 | 5.74 | 2.83 | 6.50 | 2.37 | 6.75 | 1.90 |
| 1024 | 6.29 | 2.92 | 7.36 | 2.50 | 8.50 | 2.20 |
| 2048 | 7.32 | 3.37 | 8.04 | 2.57 | 10.44 | 2.52 |
| 4096 | 7.52 | 3.21 | 10.38 | 3.16 | 13.57 | 2.96 |

### *Ammonium Copper Sulphate*, $(NH_4)_2Cu(SO_4)_2.6H_2O$

The mother solution was standardized by determining the sulphuric acid as barium sulphate, and the copper was also determined as copper oxide.

*Table VII.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 106.3 | 146.6 | 190.4 | 225.7 |
| 8 | 122.7 | 169.9 | 220.7 | 262.2 |
| 32 | 153.5 | 213.8 | 280.2 | 334.3 |
| 128 | 187.8 | 262.4 | 346.7 | 412.6 |
| 512 | 221.6 | 312.1 | 411.7 | 495.7 |
| 1024 | 236.0 | 333.5 | 442.6 | 532.5 |
| 2048 | 246.4 | 347.9 | 463.6 | 560.0 |
| 4096 | 259.4 | 367.3 | 494.0 | 597.3 |

*Table VIII.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 3.22 | 3.03 | 3.50 | 2.39 | 3.53 | 1.85 |
| 8 | 3.78 | 3.08 | 4.06 | 2.39 | 4.15 | 1.88 |
| 32 | 4.82 | 3.14 | 5.31 | 2.48 | 5.41 | 1.93 |
| 128 | 5.97 | 3.18 | 6.74 | 2.57 | 6.59 | 1.90 |
| 512 | 7.24 | 3.27 | 7.97 | 2.55 | 8.40 | 2.04 |
| 1024 | 7.80 | 3.31 | 8.73 | 2.62 | 8.99 | 2.03 |
| 2048 | 8.12 | 3.30 | 9.26 | 2.66 | 9.64 | 2.08 |
| 4096 | 8.63 | 3.33 | 10.14 | 2.76 | 10.33 | 2.09 |

### *Sodium Ferrocyanide,* $Na_4Fe(CN)_6 \cdot 12H_2O$

The mother solution was made up by direct weighing of the anhydrous salt.

*Table IX.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 136.7 | 194.9 | 259.2 | 313.4 |
| 16 | 151.3 | 215.5 | 287.0 | 347.7 |
| 32 | 167.1 | 238.5 | 318.5 | 386.2 |
| 128 | 203.5 | 289.6 | 385.9 | 464.5 |
| 512 | 234.2 | 334.1 | 446.4 | 543.2 |
| 1024 | 253.4 | 361.7 | 482.4 | 581.2 |
| 2048 | 266.4 | 380.3 | 504.0 | 612.0 |
| 4096 | 275.7 | 398.1 | 527.1 | 632.2 |

*Table X.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 4.66 | 3.41 | 5.14 | 2.64 | 5.42 | 2.09 |
| 16 | 5.14 | 3.40 | 5.72 | 2.65 | 6.07 | 2.12 |
| 32 | 5.71 | 3.42 | 6.40 | 2.68 | 6.77 | 2.13 |
| 128 | 6.89 | 3.39 | 7.70 | 2.66 | 7.86 | 2.04 |
| 512 | 7.99 | 3.41 | 8.98 | 2.69 | 9.68 | 2.17 |
| 1024 | 8.66 | 3.42 | 9.66 | 2.67 | 9.88 | 2.05 |
| 2048 | 9.11 | 3.42 | 9.90 | 2.60 | 10.80 | 2.14 |
| 4096 | 9.79 | 3.55 | 10.32 | 2.59 | 10.51 | 2.00 |

*Table XI.—Percentage Disssociation*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 49.58 | 48.96 | 49.18 | 49.57 |
| 18 | 54.88 | 54.13 | 54.45 | 55.00 |
| 32 | 60.61 | 59.91 | 60.43 | 61.00 |
| 128 | 73.81 | 72.74 | 73.21 | 73.47 |
| 512 | 84.95 | 83.92 | 84.69 | 85.92 |
| 1024 | 91.91 | 90.86 | 91.52 | 91.93 |
| 2048 | 96.63 | 95.53 | 95.62 | 96.81 |
| 4096 | 100.00 | 100.00 | 100.00 | 100.00 |

### *Potassium Sodium Sulphate,* $KNaSO_4$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

*Table XII.—Molecular Conductivity*

| V | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 88.4 | 122.5 | 159.0 | 189.6 |
| 8 | 96.1 | 146.6 | 170.6 | 209.1 |
| 32 | 113.0 | 158.1 | 207.2 | 249.7 |
| 128 | 128.8 | 179.0 | 236.1 | 284.5 |
| 512 | 135.6 | 189.6 | 250.8 | 301.0 |
| 1024 | 140.8 | 197.1 | 259.2 | 313.2 |
| 2048 | 140.9 | 198.2 | 261.4 | 316.2 |
| 4096 | 144.3 | 202.6 | 267.6 | 322.1 |

*Table XIII.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| V | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 2.73 | 3.09 | 2.92 | 2.38 | 3.06 | 1.92 |
| 8 | 4.04 | 4.30 | 1.92 | 1.30 | 3.85 | 1.79 |
| 32 | 3.68 | 3.26 | 3.93 | 2.49 | 4.25 | 2.05 |
| 128 | 4.02 | 3.12 | 4.57 | 2.55 | 4.84 | 2.05 |
| 512 | 4.32 | 3.19 | 4.90 | 2.58 | 5.02 | 2.00 |
| 1024 | 4.50 | 3.20 | 4.97 | 2.52 | 5.40 | 2.08 |
| 2048 | 4.58 | 3.25 | 5.06 | 2.55 | 5.48 | 2.10 |
| 4096 | 4.66 | 3.23 | 5.20 | 2.56 | 5.45 | 2.04 |

*Table XIV.—Percentage Dissociation*

| V | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 61.26 | 60.46 | 59.42 | 58.88 |
| 8 | 66.60 | 72.36 | 63.75 | 64.93 |
| 32 | 78.31 | 78.03 | 77.43 | 77.54 |
| 128 | 89.26 | 88.35 | 88.23 | 88.35 |
| 512 | 93.97 | 93.58 | 93.72 | 93.47 |
| 1024 | 97.57 | 97.28 | 96.86 | 97.26 |
| 2048 | 97.64 | 97.83 | 97.68 | 98.19 |
| 4096 | 100.00 | 100.00 | 100.00 | 100.00 |

### *Potassium Aluminium Sulphate*, $KAl(SO_4)_2.12H_2O$

The mother solution was standardized by determining aluminium as aluminium oxide.

*Table XV.—Molecular Conductivity*

| V | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 78.9 | 108.9 | 140.3 | 165.3 |
| 32 | 101.2 | 140.8 | 182.2 | 215.7 |
| 128 | 127.6 | 177.7 | 232.9 | 283.7 |
| 512 | 158.8 | 223.7 | 294.9 | 358.3 |
| 1024 | 177.8 | 250.5 | 332.7 | 402.8 |
| 2048 | 197.5 | 281.8 | 378.4 | 470.0 |
| 4096 | 218.8 | 314.7 | 425.5 | 528.8 |

*Table XVI.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| V | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 2.40 | 3.04 | 2.51 | 2.30 | 2.50 | 1.78 |
| 32 | 3.17 | 3.13 | 3.31 | 2.35 | 3.35 | 1.84 |
| 128 | 4.01 | 3.14 | 4.42 | 2.49 | 5.08 | 2.18 |
| 512 | 5.19 | 3.27 | 5.69 | 2.54 | 6.34 | 2.15 |
| 1024 | 5.81 | 3.27 | 6.57 | 2.62 | 7.01 | 2.11 |
| 2048 | 6.74 | 3.41 | 7.73 | 2.74 | 9.16 | 2.42 |
| 4096 | 7.67 | 3.51 | 8.86 | 2.82 | 10.33 | 2.43 |

## *Potassium Nickel Sulphate*, $K_2Ni(SO_4)_2.6H_2O$

The mother solution was standardized by determining sulphuric acid as barium sulphate and also by determining nickel as oxide.

*Table XVII.—Molecular Conductivity*

| V | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 122.6 | 170.7 | 221.9 | 265.3 |
| 32 | 155.4 | 217.0 | 283.8 | 339.7 |
| 128 | 187.5 | 263.0 | 344.8 | 414.1 |
| 512 | 219.6 | 309.3 | 407.7 | 490.7 |
| 1024 | 235.5 | 331.2 | 437.1 | 527.1 |
| 2048 | 249.5 | 349.9 | 463.0 | 560.1 |
| 4096 | 268.0 | 367.9 | 487.4 | 588.1 |

*Table XVIII.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| V | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 3.85 | 3.14 | 4.10 | 2.40 | 4.34 | 1.96 |
| 32 | 4.93 | 3.17 | 5.32 | 2.45 | 5.59 | 1.97 |
| 128 | 6.04 | 3.22 | 6.54 | 2.48 | 6.93 | 2.01 |
| 512 | 7.18 | 3.27 | 7.87 | 2.54 | 8.30 | 2.04 |
| 1024 | 7.66 | 3.25 | 8.47 | 2.56 | 9.00 | 2.06 |
| 2048 | 8.03 | 3.22 | 9.05 | 2.59 | 9.71 | 2.09 |
| 4096 | 8.57 | 3.29 | 9.56 | 2.60 | 10.07 | 2.07 |

*Table XIX.—Percentage Dissociation*

| V | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 47.01 | 46.40 | 45.53 | 45.11 |
| 32 | 59.59 | 58.98 | 58.23 | 57.76 |
| 128 | 71.89 | 71.49 | 70.74 | 70.41 |
| 512 | 84.20 | 84.07 | 83.65 | 83.44 |
| 1024 | 90.30 | 90.02 | 89.68 | 89.63 |
| 2048 | 95.67 | 95.11 | 94.99 | 95.24 |
| 4096 | 100.00 | 100.00 | 100.00 | 100.00 |

### *Potassium Chromium Sulphate* (*Violet Variety*), $KCr(SO_4)_2.12H_2O$

The mother solution was standardized by determining chromium as chromic oxide and also by determining sulphuric acid as barium sulphate.

*Table XX.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 75.8 | 105.0 | 135.3 | 159.4 |
| 16 | 87.3 | 121.2 | 157.3 | 185.3 |
| 32 | 99.0 | 138.1 | 179.6 | 211.3 |
| 128 | 127.0 | 179.5 | 236.7 | 279.9 |
| 512 | 161.1 | 232.0 | 311.5 | 374.5 |
| 1024 | 186.6 | 271.6 | 369.6 | 443.8 |
| 2048 | 213.3 | 314.2 | 428.8 | 520.6 |
| 4096 | 245.8 | 364.8 | 500.1 | 613.9 |

*Table XXI.—Temperature Coefficients*

|  | 0°–12°.5 |  | 12°.5–25° |  | 25°–35° |  |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 2.34 | 3.09 | 2.42 | 2.31 | 2.41 | 1.78 |
| 16 | 2.71 | 3.10 | 2.89 | 2.38 | 2.80 | 1.78 |
| 32 | 3.13 | 3.16 | 3.32 | 2.40 | 3.17 | 1.77 |
| 128 | 4.20 | 3.31 | 4.58 | 2.55 | 4.32 | 1.82 |
| 512 | 5.67 | 3.52 | 6.36 | 2.74 | 6.30 | 2.02 |
| 1024 | 6.80 | 3.64 | 7.84 | 2.89 | 7.42 | 2.01 |
| 2048 | 8.07 | 3.78 | 9.17 | 2.92 | 9.18 | 2.14 |
| 4096 | 9.52 | 3.87 | 10.82 | 2.97 | 11.38 | 2.28 |

### *Potassium Chromium Sulphate* (*Green Variety*)

The mother solution was prepared by heating a portion of the mother solution of the violet variety to 70° for about seven hours in a stoppered bottle.

*Table XXII.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 101.0 | 130.1 | 158.4 | 179.6 |
| 16 | 119.3 | 154.0 | 188.1 | 213.2 |
| 32 | 137.8 | 179.3 | 219.5 | 249.3 |
| 128 | 177.7 | 234.4 | 290.6 | 333.5 |
| 512 | 210.9 | 283.5 | 359.1 | 426.6 |
| 1024 | 229.7 | 310.9 | 399.6 | 479.0 |
| 2048 | 247.0 | 339.5 | 441.3 | 539.1 |
| 4096 | 273.1 | 379.4 | 500.3 | 616.2 |

*Table XXIII.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 2.33 | 2.31 | 2.26 | 1.74 | 2.12 | 1.34 |
| 16 | 2.78 | 2.33 | 2.73 | 1.77 | 2.51 | 1.33 |
| 32 | 3.32 | 2.41 | 3.22 | 1.80 | 2.98 | 1.36 |
| 128 | 4.54 | 2.55 | 4.50 | 1.92 | 4.29 | 1.48 |
| 512 | 5.81 | 2.76 | 6.05 | 2.13 | 6.75 | 1.88 |
| 1024 | 6.50 | 2.83 | 7.10 | 2.28 | 7.94 | 1.99 |
| 2048 | 7.40 | 3.00 | 8.14 | 2.40 | 9.78 | 2.22 |
| 4096 | 8.50 | 3.11 | 9.67 | 2.55 | 11.59 | 2.32 |

### *Calcium Formate*, $Ca(OOCH)_2$

The mother solution was standardized by determining calcium as the sulphate.

*Table XXIV.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 58.4 | 81.7 | 107.1 | 128.6 |
| 8 | 67.2 | 94.4 | 124.5 | 149.7 |
| 32 | 81.4 | 115.3 | 153.1 | 184.7 |
| 128 | 92.2 | 131.2 | 174.3 | 211.6 |
| 512 | 95.7 | 135.5 | 181.9 | 223.5 |
| 2048 | 101.4 | 144.6 | 190.4 | 230.6 |
| 4096 | 101.3 | 145.4 | 190.6 | 229.2 |

*Table XXV.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 1.86 | 3.19 | 2.03 | 2.49 | 2.15 | 2.01 |
| 8 | 2.18 | 3.24 | 2.41 | 2.55 | 2.52 | 2.02 |
| 32 | 2.70 | 3.32 | 3.02 | 2.62 | 3.16 | 2.06 |
| 128 | 3.12 | 3.38 | 3.45 | 2.63 | 3.73 | 2.14 |
| 512 | 3.18 | 3.32 | 3.71 | 2.74 | 4.16 | 2.29 |
| 2048 | 3.46 | 3.41 | 3.66 | 2.53 | 4.02 | 2.11 |
| 4096 | 3.53 | 3.48 | 3.62 | 2.49 | 3.86 | 2.03 |

*Table XXVI.—Percentage Dissociation*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 57.65 | 56.19 | 56.19 | 56.11 |
| 8 | 66.34 | 64.92 | 65.32 | 65.31 |
| 32 | 80.36 | 79.30 | 80.33 | 80.58 |
| 128 | 91.02 | 90.23 | 91.45 | 92.32 |
| 512 | 94.47 | 93.19 | 95.44 | 97.51 |
| 2048 | 100.00 | 99.45 | 99.89 | 100.00 |
| 4096 | .... | 100.00 | 100.00 | .... |

## *Calcium Chromate,* $CaCrO_4$

The mother solution was standardized by titrating with ferrous ammonium alum.

*Table XXVII.—Molecular Conductivity*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 57.7 | 80.9 | 105.8 | 125.4 |
| 16 | 64.6 | 90.4 | 118.5 | 140.9 |
| 32 | 72.2 | 101.4 | 133.1 | 158.2 |
| 128 | 91.2 | 126.9 | 167.5 | 200.8 |
| 512 | 106.7 | 150.0 | 198.7 | 239.5 |
| 1024 | 111.6 | 157.3 | 208.8 | 253.3 |
| 2048 | 114.4 | 160.8 | 214.0 | 264.0 |
| 4096 | 116.1 | 162.5 | 216.1 | 261.6 |

*Table XXVIII.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 1.85 | 3.21 | 1.99 | 2.46 | 1.96 | 1.85 |
| 16 | 2.06 | 3.19 | 2.25 | 2.49 | 2.24 | 1.89 |
| 32 | 2.33 | 3.23 | 2.54 | 2.51 | 2.51 | 1.89 |
| 128 | 2.86 | 3.14 | 3.25 | 2.56 | 3.33 | 1.99 |
| 512 | 3.46 | 3.24 | 3.90 | 2.60 | 4.08 | 2.05 |
| 1024 | 3.66 | 3.28 | 4.12 | 2.62 | 4.45 | 2.13 |
| 2048 | 3.71 | 3.24 | 4.26 | 2.65 | 5.00 | 2.34 |
| 4096 | 3.71 | 3.20 | 4.29 | 2.64 | 4.55 | 2.11 |

*Table XXIX—Percentage Dissociation*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 8 | 49.70 | 49.78 | 48.96 | 47.94 |
| 16 | 55.64 | 55.63 | 54.85 | 53.86 |
| 32 | 62.19 | 62.40 | 61.59 | 60.47 |
| 128 | 78.55 | 78.09 | 77.51 | 76.76 |
| 512 | 91.90 | 92.31 | 91.95 | 91.55 |
| 1024 | 96.12 | 96.80 | 96.62 | 96.83 |
| 2048 | 98.54 | 98.95 | 99.03 | 100.00 |
| 4096 | 100.00 | 100.00 | 100.00 | .... |

## *Zinc Nitrate,* $Zn(NO_3)_2.6H_2O$

The mother solution was standardized by determining zinc as zinc oxide.

*Table XXX.—Molecular Conductivity*

| *v* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 80.6 | 110.8 | 146.6 | 171.2 |
| 8 | 87.6 | 121.2 | 157.2 | 188.5 |
| 32 | 100.0 | 139.2 | 182.1 | 219.0 |
| 128 | 110.4 | 154.1 | 202.6 | 243.5 |
| 512 | 114.1 | 164.9 | 210.1 | 254.3 |
| 1024 | 117.1 | 165.0 | 216.6 | 261.3 |
| 2048 | 120.4 | 169.2 | 222.4 | 270.2 |
| 4096 | 124.4 | 175.0 | 229.1 | 279.4 |

*Table XXXI.—Temperature Coefficients*

|  | 0°–12°.5 |  | 12°.5–25° |  | 25°–35° |  |
|---|---|---|---|---|---|---|
| *v* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 2.42 | 3.00 | 2.86 | 2.58 | 2.46 | 1.68 |
| 8 | 2.69 | 3.07 | 2.88 | 2.38 | 3.13 | 1.99 |
| 32 | 3.34 | 3.34 | 3.43 | 2.46 | 3.69 | 2.03 |
| 128 | 3.50 | 3.17 | 3.88 | 2.52 | 4.09 | 2.02 |
| 512 | 4.06 | 3.56 | 3.62 | 2.20 | 4.42 | 2.10 |
| 1024 | 3.83 | 3.27 | 4.13 | 2.50 | 4.47 | 2.06 |
| 2048 | 3.90 | 3.24 | 4.26 | 2.52 | 4.78 | 2.15 |
| 4096 | 4.05 | 3.26 | 4.33 | 2.47 | 5.03 | 2.20 |

*Table XXXII.—Percentage Dissociation*

| *v* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 64.79 | 63.31 | 63.99 | 61.27 |
| 8 | 70.42 | 69.26 | 68.62 | 67.47 |
| 32 | 80.39 | 59.54 | 79.48 | 78.38 |
| 128 | 88.75 | 88.06 | 88.43 | 87.15 |
| 512 | 91.92 | 94.29 | 94.71 | 91.02 |
| 1024 | 94.13 | 94.29 | 94.54 | 93.52 |
| 2048 | 96.78 | 96.68 | 97.07 | 96.71 |
| 4096 | 100.00 | 100.00 | 100.00 | 100.00 |

### *Zinc Acetate*, $Zn(C_2H_3O_2)_2$

The mother solution was standardized by determining zinc as zinc oxide.

*Table XXXIII.—Molecular Conductivity*

| *v* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 27.8 | 38.0 | 48.0 | 55.0 |
| 8 | 37.7 | 52.2 | 66.6 | 77.2 |
| 32 | 55.5 | 78.6 | 103.0 | 122.4 |
| 128 | 70.0 | 100.7 | 134.2 | 162.1 |
| 512 | 78.6 | 113.7 | 153.2 | 185.5 |
| 1024 | 79.9 | 116.1 | 156.7 | 191.6 |
| 2048 | 83.2 | 120.8 | 163.2 | 200.1 |
| 4096 | 83.8 | 121.3 | 163.4 | 201.1 |

*Table XXXIV.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| V | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 0.81 | 2.91 | 0.80 | 2.11 | 0.70 | 1.46 |
| 8 | 1.16 | 3.08 | 1.15 | 2.20 | 1.06 | 1.59 |
| 32 | 1.85 | 3.33 | 1.95 | 2.48 | 1.94 | 1.88 |
| 128 | 2.45 | 3.50 | 2.68 | 2.66 | 2.79 | 2.08 |
| 512 | 2.81 | 3.58 | 3.16 | 2.78 | 3.23 | 2.11 |
| 1024 | 2.90 | 3.63 | 3.25 | 2.79 | 3.49 | 2.23 |
| 2048 | 3.01 | 3.61 | 3.39 | 2.81 | 3.69 | 2.26 |
| 4096 | 3.00 | 3.58 | 3.37 | 2.78 | 3.77 | 2.31 |

*Table XXXV.—Percentage Dissociation*

| V | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 33.17 | 31.33 | 29.38 | 27.35 |
| 8 | 44.99 | 43.03 | 40.76 | 38.39 |
| 32 | 66.23 | 64.80 | 63.03 | 60.87 |
| 128 | 83.53 | 83.02 | 82.13 | 80.61 |
| 512 | 93.79 | 93.73 | 93.76 | 92.24 |
| 1024 | 95.34 | 95.71 | 95.90 | 95.28 |
| 2048 | 99.28 | 99.59 | 99.86 | 99.50 |
| 4096 | 100.00 | 100.00 | 100.00 | 100.00 |

## *Lead Acetate*, $Pb(C_2H_3O_2)_2.3H_2O$

The mother solution was standardized by determining lead as lead sulphate.

*Table XXXVI.—Molecular Conductivity*

| V | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 11.2 | 16.4 | 22.1 | 27.0 |
| 8 | 16.0 | 23.3 | 31.2 | 37.8 |
| 32 | 28.8 | 41.4 | 54.9 | 66.2 |
| 128 | 46.4 | 66.3 | 87.1 | 104.2 |
| 512 | 65.3 | 92.7 | 123.1 | 146.2 |
| 1024 | 74.5 | 108.2 | 139.1 | 167.2 |
| 2048 | 84.3 | 119.4 | 156.8 | 189.1 |
| 4096 | 87.8 | 124.6 | 165.5 | 198.7 |

*Table XXXVII.—Temperature Coefficients*

| | 0°–12°.5 | | 12°.5–25° | | 25°–35° | |
|---|---|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 0.41 | 3.66 | 0.46 | 2.81 | 0.49 | 2.22 |
| 8 | 0.58 | 3.63 | 0.63 | 2.70 | 0.66 | 2.12 |
| 32 | 1.01 | 3.50 | 1.08 | 2.61 | 1.13 | 2.06 |
| 128 | 1.59 | 3.42 | 1.66 | 2.50 | 1.71 | 1.96 |
| 512 | 2.19 | 3.35 | 2.43 | 2.62 | 2.31 | 1.88 |
| 1024 | 2.70 | 3.62 | 2.47 | 2.28 | 2.81 | 2.02 |
| 2048 | 2.81 | 3.34 | 2.99 | 2.50 | 3.23 | 2.06 |
| 4096 | 2.94 | 3.35 | 3.27 | 2.62 | 3.32 | 2.15 |

*Table XXXVIII.—Percentage Dissociation*

| *V* | 0° | 12°.5 | 25° | 35° |
|---|---|---|---|---|
| 4 | 12.76 | 13.16 | 13.35 | 13.59 |
| 8 | 18.22 | 18.70 | 18.85 | 19.02 |
| 32 | 32.80 | 33.23 | 33.17 | 33.32 |
| 128 | 52.85 | 53.21 | 52.63 | 52.44 |
| 512 | 74.38 | 74.40 | 74.38 | 73.58 |
| 1024 | 84.86 | 86.84 | 84.05 | 84.15 |
| 2048 | 96.02 | 95.83 | 94.74 | 95.17 |
| 4096 | 100.00 | 100.00 | 100.00 | 100.00 |

### *Ammonium Aluminium Sulphate*, $NH_4Al(SO_4)_2.12H_2O$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

*Table XXXIX.—Molecular Conductivity*

| *V* | 35° | 50° | 65° |
|---|---|---|---|
| 8 | 168.8 | 203.5 | 236.5 |
| 16 | 202.3 | 247.5 | 288.0 |
| 64 | 261.5 | 325.8 | 384.8 |
| 128 | 284.8 | 347.5 | 426.3 |
| 512 | 365.9 | 477.5 | 573.5 |
| 2048 | 485.8 | 643.1 | 831.5 |

*Table XL.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| *V* | Cond units. | Per cent. | Cond. units | Per cent. |
| 8 | 2.31 | 1.37 | 2.20 | 1.08 |
| 16 | 3.01 | 1.48 | 2.70 | 1.09 |
| 64 | 4.29 | 1.64 | 3.93 | 1.21 |
| 128 | 4.18 | 1.47 | 5.25 | 1.51 |
| 512 | 7.44 | 2.03 | 6.40 | 1.34 |
| 2048 | 10.49 | 2.16 | 12.56 | 1.95 |

### *Disodium Phosphate,* $HNa_2PO_4.12H_2O$

The mother solution was standardized by determining the phosphoric acid as magnesium pyrophosphate.

*Table XLI.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 8 | 141.8 | 61.8 | 184.1 | 61.5 | 228.0 | 60.6 |
| 32 | 176.8 | 77.0 | 228.2 | 76.3 | 287.9 | 76.6 |
| 128 | 206.5 | 90.0 | 269.0 | 89.8 | 334.4 | 88.9 |
| 512 | 224.3 | 97.8 | 292.7 | 97.8 | 376.1 | 100.0 |
| 2048 | 229.5 | 100.0 | 299.3 | 100.0 | (355.4) | |

*Table XLII.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 2.82 | 1.99 | 2.93 | 1.59 |
| 32 | 3.43 | 1.94 | 3.98 | 1.74 |
| 128 | 4.17 | 2.02 | 4.36 | 1.62 |
| 512 | 4.56 | 2.03 | 5.56 | 1.90 |
| 2048 | 4.65 | 2.03 | 4.65 | .... |

### *Sodium Tetraborate,* $Na_2B_4O_7.5H_2O$

The mother solution was standardized as the anhydrous salt.

*Table XLIII.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 16 | 141.3 | 70.9 | 182.8 | 67.6 | 231.3 | 64.4 |
| 32 | 157.1 | 78.8 | 204.0 | 75.5 | 256.2 | 71.3 |
| 128 | 172.4 | 86.5 | 224.1 | 82.9 | 281.6 | 78.4 |
| 512 | 186.7 | 93.6 | 247.8 | 91.7 | 316.7 | 88.1 |
| 2048 | 199.4 | 100.0 | 270.3 | 100.0 | 359.3 | 100.0 |

*Table XLIV.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 16 | 2.77 | 1.96 | 3.23 | 1.76 |
| 32 | 3.13 | 1.99 | 3.48 | 1.71 |
| 128 | 3.45 | 2.00 | 3.83 | 1.71 |
| 512 | 4.01 | 2.15 | 4.59 | 1.85 |
| 2048 | 4.73 | 2.37 | 5.93 | 2.19 |

### *Potassium Aluminium Sulphate*, $KAl(SO_4)_2.12H_2O$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

*Table XLV.—Molecular Conductivity*

| V | 35° | 50° | 65° |
|---|---|---|---|
| 4 | 142.3 | 172.5 | 196.1 |
| 8 | 165.3 | 207.5 | 240.6 |
| 32 | 215.7 | 255.1 | 317.4 |
| 128 | 283.7 | 356.9 | 426.2 |
| 512 | 358.3 | 446.9 | 557.1 |
| 2048 | 470.0 | 626.4 | 796.4 |

*Table XLVI.—Temperature Coefficients*

| | 35°-50° | | 50°-65° | |
|---|---|---|---|---|
| V | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 2.01 | 1.41 | 1.57 | 0.87 |
| 8 | 2.81 | 1.70 | 2.21 | 1.06 |
| 32 | 2.63 | 1.22 | 4.15 | 1.63 |
| 128 | 4.88 | 1.72 | 4.62 | 1.29 |
| 512 | 5.91 | 1.65 | 7.35 | 1.64 |
| 2048 | 10.42 | 2.22 | 11.33 | 1.81 |

### *Potassium Sulphocyanate*, KCNS

The mother solution was prepared by direct weighing.

*Table XLVII.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| V | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 4 | 127.6 | 79.2 | 160.2 | 77.6 | 191.1 | 76.2 |
| 8 | 132.9 | 82.4 | 166.7 | 80.8 | 201.8 | 80.4 |
| 32 | 142.3 | 88.3 | 179.6 | 87.0 | 219.6 | 87.5 |
| 128 | 149.3 | 92.6 | 190.0 | 92.1 | 232.4 | 92.6 |
| 512 | 153.7 | 95.4 | 192.6 | 93.3 | 239.3 | 95.4 |
| 2048 | 161.2 | 100.0 | 206.4 | 100.0 | 250.9 | 100.0 |

*Table XLVIII.—Temperature Coefficients*

| | 35°-50° | | 50°-65° | |
|---|---|---|---|---|
| V | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 2.17 | 1.70 | 2.06 | 1.29 |
| 8 | 2.25 | 1.69 | 2.34 | 1.40 |
| 32 | 2.49 | 1.75 | 2.67 | 1.49 |
| 128 | 2.74 | 1.84 | 2.83 | 1.49 |
| 512 | 2.60 | 1.69 | 3.11 | 1.62 |
| 2048 | 3.01 | 1.86 | 2.97 | 1.44 |

Vol. 4
191

### *Monopotassium Phosphate,* $H_2KPO_4$

The mother solution was standardized by determining phosphoric acid as magnesium pyrophosphate.

*Table XLIX.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 8 | 310.4 | 63.8 | 391.6 | 64.5 | 477.2 | 61.2 |
| 32 | 380.0 | 78.1 | 481.2 | 79.2 | 588.4 | 75.5 |
| 128 | 424.3 | 87.2 | 537.6 | 88.5 | 661.2 | 84.8 |
| 512 | 452.3 | 93.0 | 573.1 | 94.4 | 708.2 | 90.9 |
| 2048 | 471.5 | 96.9 | 599.9 | 98.8 | 740.9 | 95.1 |
| 8192 | 486.4 | 100.0 | 621.4 | 100.0 | 779.4 | 100.0 |

*Table L.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 8 | 5.41 | 1.74 | 5.71 | 1.46 |
| 32 | 6.75 | 1.78 | 7.15 | 1.49 |
| 128 | 7.55 | 1.78 | 8.24 | 1.53 |
| 512 | 8.05 | 1.78 | 9.01 | 1.57 |
| 2048 | 8.56 | 1.81 | 9.40 | 1.58 |
| 8192 | 9.00 | 1.82 | 10.53 | 1.69 |

### *Potassium Acetate,* $KC_2H_3O_2$

The mother solution was standardized by determining potassium as the sulphate.

*Table LI.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 4 | 94.4 | 75.40 | 125.6 | 78.84 | 142.1 | 72.13 |
| 8 | 102.7 | 82.03 | 131.6 | 82.61 | 160.4 | 81.42 |
| 32 | 112.0 | 89.46 | 147.0 | 92.28 | 180.8 | 91.78 |
| 128 | 118.7 | 94.81 | 154.6 | 97.05 | 184.5 | 93.66 |
| 512 | 125.2 | 100.00 | 159.3 | 100.00 | 194.9 | 98.94 |
| 2048 | 123.3 | .... | 157.7 | .... | 197.0 | 100.00 |

*Table LII.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 2.08 | 2.20 | 1.10 | 0.88 |
| 8 | 1.93 | 1.88 | 1.92 | 1.46 |
| 32 | 2.33 | 2.08 | 2.25 | 1.53 |
| 128 | 2.40 | 2.02 | 2.00 | 1.29 |
| 512 | 2.27 | 1.81 | 2.37 | 1.49 |
| 2048 | 2.29 | 1.86 | 2.62 | 1.66 |

### *Calcium Chloride*, $CaCl_2.6H_2O$

The mother solution was standardized by determining calcium as carbonate and chlorine by Mohr's method.

*Table LIII.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 4 | 189.1 | 63.41 | 237.7 | 62.22 | 290.4 | 61.16 |
| 8 | 208.1 | 69.78 | 258.5 | 67.67 | 318.7 | 67.12 |
| 32 | 242.0 | 81.16 | 306.5 | 80.24 | 378.5 | 79.72 |
| 128 | 267.1 | 89.57 | 340.8 | 89.21 | 418.9 | 88.22 |
| 512 | 283.5 | 95.07 | 362.4 | 94.87 | 452.5 | 95.30 |
| 2048 | 298.2 | 100.0 | 382.0 | 100.00 | 474.8 | 100.00 |

*Table LIV.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 3.24 | 1.71 | 3.51 | 1.48 |
| 8 | 3.36 | 1.62 | 4.01 | 1.55 |
| 32 | 4.30 | 1.78 | 4.80 | 1.57 |
| 128 | 4.91 | 1.84 | 5.21 | 1.53 |
| 512 | 5.26 | 1.86 | 6.01 | 1.66 |
| 2048 | 5.59 | 1.88 | 6.19 | 1.62 |

### *Magnesium Chloride*, $MgCl_2.6H_2O$

The mother solution was standardized by determining magnesium as magnesium pyrophosphate and chlorine by Mohr's method.

*Table LV.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 4 | 179.8 | 62.17 | 228.0 | 61.09 | 280.6 | 60.27 |
| 8 | 196.5 | 67.95 | 249.7 | 66.91 | 303.8 | 65.25 |
| 32 | 231.6 | 80.08 | 294.7 | 78.97 | 364.8 | 78.35 |
| 128 | 249.8 | 86.37 | 311.8 | 83.55 | 401.6 | 86.25 |
| 512 | 269.9 | 91.20 | 348.3 | 93.33 | 433.1 | 93.02 |
| 2048 | 289.2 | 100.00 | 373.2 | 100.00 | 465.6 | 100.00 |

*Table LVI.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 3.21 | 1.79 | 3.51 | 1.54 |
| 8 | 3.55 | 1.81 | 3.61 | 1.45 |
| 32 | 4.21 | 1.82 | 4.67 | 1.58 |
| 128 | 4.13 | 1.65 | 5.93 | 1.90 |
| 512 | 5.23 | 1.94 | 5.65 | 1.62 |
| 2048 | 5.60 | 1.94 | 6.16 | 1.65 |

### *Manganese Sulphate,* $MnSO_4.4H_2O$

The mother solution was standardized by determining manganese as manganous pyrophosphate and sulphuric acid as barium sulphate.

*Table LVII.—Molecular Conductivity*

| $V$ | 35° | 50° | 65° |
|---|---|---|---|
| 4 | 78.0 | 88.0 | 108.3 |
| 8 | 92.6 | 112.8 | 130.0 |
| 32 | 128.5 | 156.4 | 181.8 |
| 128 | 166.7 | 204.1 | 241.9 |
| 512 | 219.4 | 277.5 | 338.7 |
| 2048 | 246.0 | 326.7 | 404.6 |

*Table LVIII.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 0.67 | 0.86 | 1.35 | 1.53 |
| 8 | 1.35 | 1.46 | 1.15 | 1.04 |
| 32 | 1.86 | 1.45 | 1.69 | 1.08 |
| 128 | 2.49 | 1.49 | 2.52 | 1.24 |
| 512 | 3.87 | 1.76 | 4.08 | 1.47 |
| 2048 | 5.38 | 2.19 | 5.19 | 1.59 |

### *Ferric Chloride*, $FeCl_3.6H_2O$

The mother solution was standardized by determining iron as ferric oxide.

*Table LIX.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 4 | 214.3 | 16.92 | 269.5 | 17.71 | 327.0 | 19.39 |
| 8 | 276.5 | 21.83 | 346.9 | 23.32 | .... | .... |
| 32 | 424.7 | 33.52 | 515.8 | 34.68 | .... | .... |
| 128 | 827.1 | 65.29 | 1037.6 | 69.75 | 1512.5 | 89.71 |
| 512 | 1050.7 | 82.94 | 1405.4 | 94.48 | 1685.9 | 100.00 |
| 2048 | 1266.8 | 100.00 | 1487.5 | 100.00 | 1673.6 | .... |

*Table LX.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 3.68 | 1.72 | 3.83 | 1.42 |
| 8 | 4.69 | 1.70 | .... | .... |
| 32 | 6.07 | 1.43 | .... | .... |
| 128 | 14.00 | 1.69 | 31.7 | 3.85 |
| 512 | 23.6 | 2.25 | 18.7 | 1.33 |
| 2048 | 14.7 | 1.60 | 12.4 | 0.83 |

### *Chromium Sulphate* (*Green Variety*)

The mother solution was standardized by determining chromium as chromic oxide.

*Table LXI.—Molecular Conductivity*

| $V$ | 35° | 50° | 65° |
|---|---|---|---|
| 4 | 128.2 | 160.0 | 189.6 |
| 8 | 183.5 | 227.8 | 262.9 |
| 32 | 302.0 | 354.4 | 417.4 |
| 128 | 433.9 | 522.7 | 606.0 |
| 512 | 673.3 | 811.1 | 977.3 |
| 2048 | 961.1 | 1207.8 | 1534.7 |

*Table LXII.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 2.12 | 1.65 | 1.97 | 1.23 |
| 8 | 2.95 | 1.61 | 2.34 | 1.03 |
| 32 | 3.49 | 1.16 | 4.20 | 1.19 |
| 128 | 5.92 | 1.34 | 5.55 | 1.06 |
| 512 | 9.19 | 1.37 | 11.08 | 1.37 |
| 2048 | 16.45 | 1.71 | 21.79 | 1.80 |

## *Nickel Nitrate*, $Ni(NO_3)_2.6H_2O$

The mother solution was standardized by determining nickel as nickel oxide.

*Table LXIII.—Molecular Conductivity and Dissociation*

| | 35° | | 50° | | 65° | |
|---|---|---|---|---|---|---|
| $V$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ | $\mu_v$ | $\alpha$ |
| 4 | 200.8 | 61.0 | 252.4 | 60.1 | 306.6 | 59.4 |
| 8 | 216.8 | 65.8 | 276.3 | 65.6 | 343.5 | 66.6 |
| 32 | 260.1 | 79.0 | 330.3 | 78.6 | 402.4 | 78.0 |
| 128 | 289.7 | 89.8 | 369.2 | 87.9 | 453.2 | 87.8 |
| 512 | 314.2 | 95.4 | 399.7 | 95.2 | 494.8 | 95.9 |
| 2048 | 329.3 | 100.0 | 420.0 | 100.0 | 516.0 | 100.0 |

*Table LXIV.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 3.44 | 1.71 | 3.61 | 1.43 |
| 8 | 3.97 | 1.83 | 4.48 | 1.62 |
| 32 | 4.68 | 1.80 | 4.81 | 1.46 |
| 128 | 5.30 | 1.83 | 5.60 | 1.52 |
| 512 | 5.70 | 1.81 | 6.34 | 1.59 |
| 2048 | 6.05 | 1.84 | 6.40 | 1.52 |

## *Nickel Sulphate*, $NiSO_4.6H_2O$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

*Table LXV.—Molecular Conductivity*

| $V$ | 35° | 50° | 65° |
|---|---|---|---|
| 4 | 78.6 | 95.5 | 111.8 |
| 8 | 93.1 | 115.5 | 135.7 |
| 32 | 127.0 | 158.2 | 187.8 |
| 128 | 171.8 | 215.6 | 259.8 |
| 512 | 219.4 | 278.9 | 339.7 |
| 2048 | 264.0 | 341.3 | 425.7 |

*Table LXVI.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| $V$ | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 1.13 | 1.44 | 1.09 | 1.14 |
| 8 | 1.49 | 1.60 | 1.35 | 1.17 |
| 32 | 2.08 | 1.64 | 1.97 | 1.25 |
| 128 | 2.92 | 1.70 | 2.95 | 1.37 |
| 512 | 3.97 | 1.81 | 4.05 | 1.45 |
| 2048 | 5.15 | 1.95 | 5.63 | 1.65 |

### *Cobalt Sulphate,* $CoSO_4.7H_2O$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

*Table LXVII.—Molecular Conductivity*

| *V* | 35° | 50° | 65° |
|---|---|---|---|
| 4 | 80.0 | 95.6 | 112.7 |
| 8 | 94.9 | 117.2 | 137.5 |
| 32 | 129.1 | 160.0 | 189.6 |
| 128 | 172.5 | 203.4 | 256.6 |
| 512 | 229.8 | 290.7 | 346.0 |
| 2048 | 264.8 | 340.3 | 421.6 |

*Table LXVIII.—Temperature Coefficients*

| | 35°–50 | | 50°–65° | |
|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 1.04 | 1.30 | 1.14 | 1.19 |
| 8 | 1.49 | 1.57 | 1.35 | 1.15 |
| 32 | 2.06 | 1.59 | 1.97 | 1.23 |
| 128 | 2.06 | 1.19 | 3.55 | 1.74 |
| 512 | 4.06 | 1.76 | 3.49 | 1.20 |
| 2048 | 5.03 | 1.90 | 5.42 | 1.59 |

### *Copper Sulphate,* $CuSO_4.5H_2O$

The mother solution was standardized by determining copper as copper oxide and sulphuric acid as barium sulphate.

*Table LXIX.—Molecular Conductivity*

| *V* | 35° | 50° | 65° |
|---|---|---|---|
| 4 | 75.6 | 93.8 | 107.4 |
| 8 | 90.5 | 109.1 | 124.5 |
| 32 | 126.1 | 152.7 | 173.8 |
| 128 | 170.7 | 210.3 | 247.3 |
| 512 | 222.7 | 279.1 | 337.7 |
| 2048 | 266.3 | 343.3 | 422.7 |

*Table LXX.—Temperature Coefficients*

| | 35°–50° | | 50°–65° | |
|---|---|---|---|---|
| *V* | Cond. units | Per cent. | Cond. units | Per cent. |
| 4 | 1.21 | 1.60 | 0.91 | 0.97 |
| 8 | 1.24 | 1.37 | 1.02 | 0.93 |
| 32 | 1.77 | 1.40 | 1.41 | 0.92 |
| 128 | 2.64 | 1.55 | 2.45 | 1.16 |
| 512 | 3.76 | 1.69 | 3.91 | 1.40 |
| 2048 | 5.13 | 1.93 | 5.29 | 1.54 |

## DISCUSSION OF RESULTS

### *Salts Studied from 0° to 35°*

The conductivity data (Tables XXIV to XXXVIII) for the salts derived from diacid bases are of the same general character. This is best seen by drawing curves. Fig. I shows conductivity-concentration curves for zinc acetate, which may be taken as an example of these salts. The diagrams for the other members of the group are similar, except that the curve is much flattened in the cases of lead acetate and calcium chromate. This is apparent in Fig. II, which gives the conductivity-concentration curves for lead acetate.

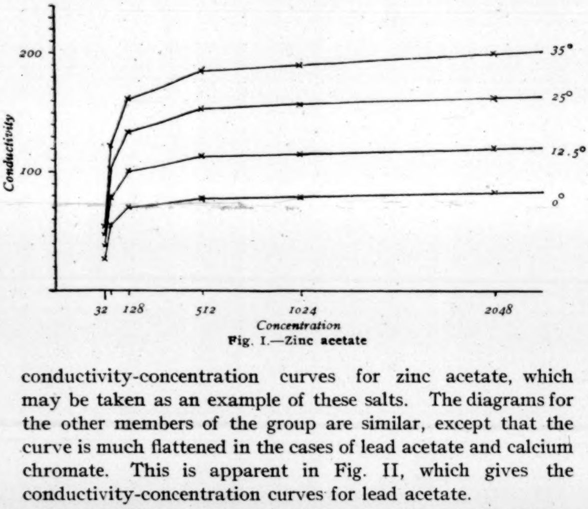


Fig. I.—Zinc acetate

Lead acetate presents a number of exceptions. In concentrated solutions it has the smallest molecular conductivity and dissociation of any of the salts studied. At infinite dilution, however, the conductivity is nearly the same at all temperatures as for zinc acetate. Again, lead acetate shows the smallest temperature coefficients of conductivity at high temperatures, and the most rapid increase with dilution of any of the salts brought within the scope of this investigation.

It has been known that dissociation seems to be nearly independent of temperature over the range of temperature at which our work was done, but in general decreases as the temperature rises. This is true of all but four of the salts included in this investigation.

The four apparent exceptions are potassium acetate, calcium formate, lead acetate and sodium ferrocyanide. Potassium acetate shows no well-marked change in the dissociation with temperature. Dissociation apparently increases as the temperature rises in the cases of calcium formate and sodium ferrocyanide. The same is true of lead acetate in concentrated solutions. It is intended to study farther the dissociation of these apparently exceptional salts.

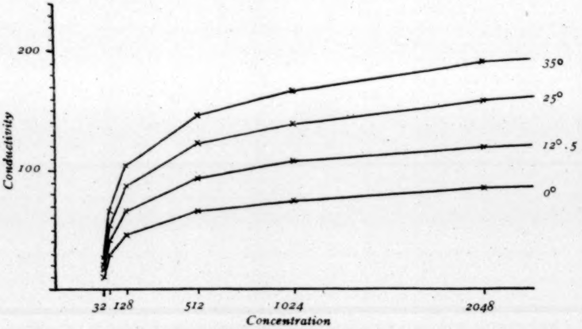


Fig. II.—Lead acetate

The complex salt sodium ferrocyanide has high conductivity and large temperature coefficients of conductivity. The percentage coefficients are remarkably constant at the various dilutions. The value for $\mu_\infty$ was hardly reached at the highest dilution used, which is probably due, in part at least, to the breaking down into simpler ions in the more dilute solutions. Hydrolysis also probably takes place.

The remaining salts studied over the lower range in temperature are double salts and all are sulphates. Ammonium copper sulphate and potassium nickel sulphate yield very similar conductivity data. In the stronger solutions the nickel salt shows the greater conductivity, but at higher dilution the molecular conductivity and the temperature coefficients of these two salts are almost identical. Conductivity in these cases is probably somewhat affected by hydrolysis.

A comparison of the data for the violet and green varieties of ammonium chrome alum shows that in the more concentrated solutions the green variety has much higher conductivity. At higher dilutions the reverse is true; the violet conducts better than the green form. The same general relation is shown in the case of potassium chrome alum, though $\mu_v$ for the green variety does not actually fall below the $\mu_v$ value for the violet form at the highest dilution employed. This relation between the two varieties appears in Fig. III.

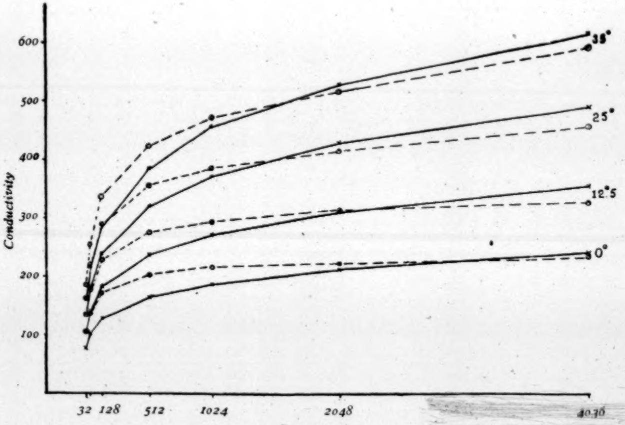


**Fig. III.—Ammonium chromium sulphate** { —×—×—× **Violet variety**; --(•)--(•)--(•)-- **Green variety** }

The violet form of the chromium salts is transformed into the green variety by heating the solid salt or its solution for some time at about 70°. The relation between the two forms has been the subject of many investigations. Monti[1] observed that the change was accompanied by an increase in the conductivity of the solution. Recoura,[2] in an elaborate investigation, explained the change as hydrolytic, resulting in the formation of free sulphuric acid and a basic salt. This conclusion was confirmed by Whitney.[3] Jones and Mackay[4] showed by conductivity measurements that the transformation was continuous as the temperature rose slowly from 37°·5 to 90°.

In the light of the conclusions of these workers, the explanation of the relative conductivity of the two forms of ammonium chrome alum would seem to be that the green modification, by virtue of the hydrolysis caused by heating, has the higher initial conductivity, but when diluted it is incapable of further hydrolysis to the same extent as appears to occur in the case of the normal violet variety.

### *Salts Studied from 35° to 65°*

Before considering in detail the salts studied from 35° to 65° some general relations should be discussed. It was found by Jones and Ota[5] and by Jones and Knight[6] that concentrated solutions of certain salts in water often show abnormally great depressions of the freezing point of the solvent. It was also shown to be true in many cases that the molecular lowering of the freezing point increased from a certain concentration both with dilution and with increased concentration. The subject was further studied by Jones and Chambers[7] and by Jones and Getman.[8] It was found that the molecular conductivities of solutions of the substances which showed a minimum in the value of the molecular lowering were perfectly normal at all concentrations.

---

[1] Z. anorg. Chem., **12,** 75 (1896).

[2] Ann. chim. phys., [7] **4,** 494 (1895).

[3] Z. physik. Chem., **20,** 40 (1896).

[4] This Journal, **19,** 103 (1897).

[5] *Ibid.*, **22,** 5 (1899).

[6] *Ibid.*, **22,** 110 (1899).

[7] *Ibid.*, **23,** 89 (1900).

[8] Z. physik. Chem., **46,** 244 (1903).

To account for the facts, Jones[1] offered the suggestion that the molecules of the dissolved substance form complex compounds or hydrates with a portion of the water, thus virtually increasing the concentration of the solution. The freezing point is thus abnormally depressed. It was also pointed out that substances which give these abnormal results are often hygroscopic and that, when dehydrated, they readily combine with water. Jones and his assistants have collected a large amount of evidence,[2] by several independent methods, which supports the theory of hydration. A method[3] was developed by which the approximate composition of the hydrates of many substances was calculated.

It was pointed out by Jones[4] that the breaking down of the hydrated molecules, or of the hydrated ions, by a rise in temperature would diminish the mass of the ion and thus increase the conductivity. The more complex the hydrates the greater would be the change in hydration and, consequently, the greater the change in conductivity. Therefore "we should expect to find *those ions with the largest hydrating power having the largest temperature coefficients of conductivity.*"[5] An examination of the experimental results of Jones and West[6] led to the following conclusions:

1. The temperature coefficients of conductivity of aqueous solutions of electrolytes are greater, the greater the hydrating power of the electrolyte.

2. The temperature coefficients of conductivity of aqueous solutions of electrolytes are of the same order of magnitude for those substances having, approximately, the same hydrating power.

3. The temperature coefficients of conductivity, for any given substance, increase with the dilution of the solution, and the increase is greatest for those substances with large hydrating power.[7]

---

[1] THIS JOURNAL, **23**, 103 (1900).

[2] See Hydrates in Aqueous Solution; Carnegie Institution of Washington, Publication No. **60**.

[3] *Ibid.*, pp. 28–145.

[4] THIS JOURNAL, **35**, 445 (1906).

[5] *Loc. cit.*, p. 447.

[6] THIS JOURNAL, **34**, 357 (1905).

[7] *Ibid.*, **35**, 450 (1906).

Similar results were obtained by Jones and Clover.[1]

The composition of the hydrates formed by some of the substances which were brought within the scope of this investigation has been approximately determined by Jones[2] and his assistants. In general, the hydrating power may be taken as roughly proportional to the amount of water of crystallization.

The substances named in Table LXXI crystallize with little or no water, and have slight hydrating power. They are seen to have small temperature coefficients of conductivity. The substances named in Table LXXII have large hydrating power and also have large temperature coefficients of conductivity.

*Table LXXI.—Substances with Slight Hydrating Power*

| | Temperature coefficients in conductivity units | | | | |
|---|---|---|---|---|---|
| | *V* | | *V* | | Temp. range |
| KCNS | 4 | 2.17 | 2048 | 3.01 | 35°–50° |
| $KC_2H_3O_2$ | 4 | 2.08 | 2048 | 2.29 | 35°–50° |
| $Ca(OOCH)_2$ | 4 | 2.15 | 2048 | 4.02 | 25°–35° |
| $Zn(C_2H_3O_2)_2$ | 4 | 0.70 | 2048 | 3.69 | 25°–35° |
| $Pb(C_2H_3O_2)_2.3H_2O$ | 4 | 0.49 | 2048 | 3.23 | 25°–35° |
| $CaCrO_4.2H_2O$ | 8 | 1.96 | 2048 | 5.00 | 25°–35° |

*Table LXXII.—Substances with Large Hydrating Power*

| | Temperature coefficients in conductivity units | | | | |
|---|---|---|---|---|---|
| | *V* | | *V* | | Temp. range |
| $Ni(NO_3)_2.6H_2O$ | 4 | 3.44 | 2048 | 6.05 | 35°–50° |
| $CaCl_2.6H_2O$ | 4 | 3.24 | 2048 | 5.59 | 35°–50° |
| $MgCl_2.6H_2O$ | 4 | 3.21 | 2048 | 5.60 | 35°–50° |
| $Zn(NO_3)_2.6H_2O$ | 4 | 2.46 | 2048 | 4.78 | 25°–35° |
| $FeCl_3.6H_2O$ | 4 | 3.68 | 2048 | 14.7 | 35°–50° |
| $HNa_2PO_4.12H_2O$ | 8 | 2.82 | 2048 | 4.65 | 35°–50° |
| $H_2KPO_4$ | 8 | 5.41 | 2048 | 8.56 | 35°–50° |
| $Na_2B_4O_7.5H_2O$ | 16 | 2.77 | 2048 | 4.73 | 35°–50° |

The values used in these tables are not strictly comparable, since the concentrations and the ranges of temperatures at which the temperature coefficients were determined are not the same throughout, but the agreement is sufficiently close to warrant their use in showing the general relations.

---

[1] THIS JOURNAL, **43**, 215 (1906).

[2] Hydrates in Aqueous Solution; Carnegie Institution of Washington, No. **60**.

Our results confirm the conclusion of Jones cited above, and are in perfect accord with the theory of hydration advanced by him.

The sulphates which we have studied in this investigation are omitted from Tables LXXI and LXXII, because, as shown by Jones and his coworkers,[1] the sulphates usually show abnormal results. In general, sulphates have very small temperature coefficients of conductivity, and appear to have small hydrating power in solution. There is evidence that some sulphates, at least, are polymerized in concentrated solutions.

Sodium tetraborate gives normal conductivity results at 35°, but at higher temperatures the increase in conductivity with dilution is exceptionally rapid. The salt also has large temperature coefficients of conductivity, and is undoubtedly hydrated in solution. Boric acid being little dissociated and, therefore, a weak acid, the sodium salt would certainly undergo hydrolysis. By assuming both hydration and hydrolysis to take place, the behavior of the salt is easily accounted for. At the lower temperatures the hydrolysis, due to increasing dilution, is balanced by the increasing complexity of the fairly stable hydrates. As the temperature rises the hydrates break down, while hydrolysis continues unchecked so that the conductivity increases rapidly.

Calcium and magnesium chlorides give almost identical results, except that the molecular conductivity of the calcium salt is about ten conductivity units above that of magnesium chloride. The latter salt shows greater increase in the value of $\mu_v$ with dilution at 56°, which accords with its greater hydration, as shown by Jones and Bassett.[2]

Nickel nitrate also shows large temperature coefficients. It is known[3] to possess marked power of hydration.

The conductivity data for the sulphates of nickel, cobalt, copper, and manganese are remarkably similar in every respect. There is little indication of an approach to $\mu_\infty$ at the highest dilution employed. The temperature coefficients are not large in concentrated solutions, but increase rapidly with dilution. This behavior is probably due, in part at least, to the polymerization of the sulphates in concentrated solutions.

---

[1] Hydrates in Aqueous Solution; Carnegie Institution of Washington, Publication No. **60**, pp. 80, 136, 148.

[2] THIS JOURNAL, **33**, 555 (1905).

[3] Jones: Hydrates in Aqueous Solution; Carnegie Institution of Washington, Publication No. **60**, p. 78.

The molecular conductivity of the quaternary electrolytes, chromium sulphate and ferric chloride, increases very rapidly with dilution and also, in dilute solutions, with rise in temperature. Hydrolysis undoubtedly plays a prominent part. In the case of ferric chloride distinct precipitation, due to hydrolysis, occurred at 65° in the N/8 and N/32 solutions. The conductivity curve of this salt is interesting (Fig. IV).

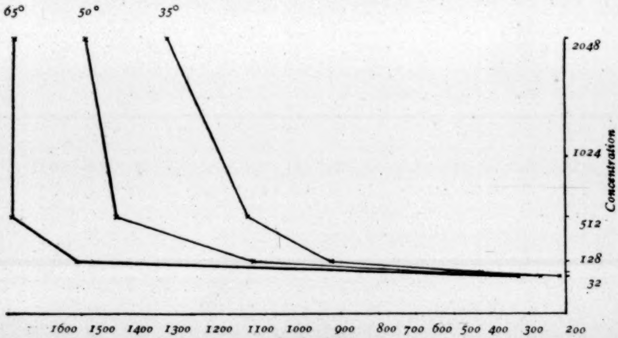


**Fig. IV.—Ferric chloride**

The abrupt bend in the curve for 50° and 65° at the N/512 concentration indicates that the cause of the increasing conductivity—presumably hydrolysis—is rapidly becoming less effective. It would seem that under these conditions of temperature and dilution the hydrolysis of the salt is very great.

The ammonium and potassium alums were studied through both ranges of temperature (0°–35° and 35°–65°), and the values of $\mu_v$ recorded for 35° were deduced from all the readings made at this temperature. Fig. V shows the conductivity-temperature curves for potassium alum through the entire range of temperature. In strong solutions, at ordinary

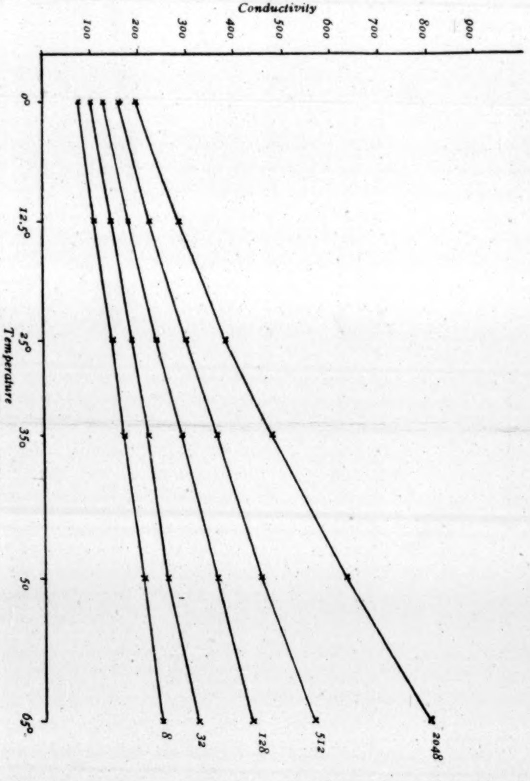


Fig. V.—Potassium aluminium sulphate

temperatures, molecular conductivity is nearly a linear function of temperature; but at greater dilutions the curve in parabolic.[1] All of the salts studied in this investigation yield conductivity-temperature curves of this same general character.

The condition of double salts, when in solution, presents a problem of interest. Investigators have sought for evidence which would decide whether such salts, when dissolved, break down into their constituent salts, which then dissociate in the usual way; or whether they ionize to some extent as salts of complex acids. Four investigations[2] bearing on the general problem have been carried out in this laboratory. Jones and Mackay compared the conductivity of certain alums with the sum of the conductivities of the constituent salts. They found the conductivity of the alums in dilute solutions to be almost the same as the sum of the conductivities of the components. In concentrated solutions the alums were found to have a conductivity less than the sum of the conductivities of the components, and the difference increased with the concentration. The difference was greater than that observed when mixtures of sulphates incapable of forming double salts were compared. Similar methods were used by the other workers. The general conclusion from these researches was that the double salts in moderately concentrated solutions are not wholly broken down into the simple salts.

In these investigations the conductivities were measured at 25°. As we now have at hand conductivity data over a considerable range in temperature, it appears to be of interest to apply the method of Jones and Mackay at other temperatures.

The following is the table of Jones and Mackay[3] giving the comparisons for potassium alum at 25°:

---

[1] Jones and Jacobson: THIS JOURNAL, **40,** 402 (1908). White and Jones: *Ibid.*, **44,** 199 (1910).

[2] Jones and Mackay: *Ibid.*, **19,** 83 (1897). Jones and Ota: *Ibid.*, **22,** 5 (1899). Jones and Knight: *Ibid.*, **22,** 110 (1899). Jones and Caldwell: *Ibid.*, **25,** 349 (1901).

[3] *Ibid.*, **34,** 357 (1905).

*Table LXXIII.—Potassium Alum, 25° (Jones and Mackay)*

| *V* | $K_2SO_4$ | $Al_2(SO_4)_3$ | *Sum/2* | $KAlSO_4$ | Diff. Per cent. |
|---|---|---|---|---|---|
| 5 | 172.7 | 108.0 | 140.3 | 133.9 | —4.5 |
| 8 | 183.3 | 124.2 | 153.7 | 149.2 | —3.0 |
| 20 | 205.1 | 158.1 | 181.6 | 178.3 | —1.7 |
| 40 | 220.3 | 185.7 | 203.0 | 202.5 | —0.2 |
| 200 | 252.4 | 290.4 | 271.4 | 269.0 | —0.8 |
| 400 | 262.2 | 342.6 | 302.4 | 305.2 | +0.9 |

This may be compared with Table LXXIV, which gives the corresponding relations at 0°, 35°, and 65°. The values of the conductivity of aluminum sulphate were kindly furnished by Miss L. G. Winston. The conductivity values of potassium sulphate are taken from the work of Jones and West.[1]

*Table LXXIV.—Potassium Alum*

| *V* | $K_2SO$ | $Al_2(SO_4)_3$ | *Sum/2* | $KAlSO_4$ | Diff. | Diff. Per cent. |
|---|---|---|---|---|---|---|
| | | | 0° | | | |
| 8 | 101.9 | 65.2 | 83.6 | 78.9 | —4.7 | —5.6 |
| 32 | 117.9 | 89.5 | 103.7 | 101.2 | —2.5 | —2.4 |
| 128 | 131.9 | 121.8 | 126.9 | 127.6 | +0.7 | +0.5 |
| 512 | 142.7 | 164.1 | 153.4 | 158.8 | +5.4 | +3.5 |
| | | | 35° | | | |
| 8 | 220.3 | 137.2 | 178.8 | 165.3 | —13.5 | —7.5 |
| 32 | 259.7 | 197.1 | 228.4 | 215.7 | —12.7 | —5.5 |
| 128 | 296.9 | 274.1 | 285.5 | 283.7 | — 1.8 | —0.6 |
| 512 | 319.6 | 388.1 | 353.9 | 358.3 | + 4.4 | +1.2 |
| | | | 65° | | | |
| 8 | 332.8 | 188.4 | 260.6 | 240.6 | —20.0 | —7.7 |
| 32 | 400.0 | 264.6 | 332.3 | 317.4 | —14.9 | —4.5 |
| 218 | 456.2 | 387.6 | 421.9 | 426.2 | + 4.3 | —1.0 |
| 512 | 500.7 | 581.6 | 541.1 | 557.1 | +16.0 | +2.9 |

Our values for "difference" in per cent. are of the same order of magnitude as those obtained by Jones and Mackay, and confirm their conclusions. It is noticeable that the percentage differences are nearly the same at the various temperatures. This may be regarded as evidence that the breaking down of potassium alum in solution is little affected by temperature, which, from other evidence, is known to be true of dissociation in general.

---

[1] THIS JOURNAL, **34**, 357 (1905).

In Table LXXV, from the work of Jones and Caldwell,[1] the conductivity of the double salt, potassium nickel sulphate, is compared with the sum of the conductivities of the components, all measurements being made at 25°. Table LXXVI shows the same relations for this salt at 0° and 35°. The values for the conductivity of nickel sulphate given in Table LXXVI are taken from the work of Jones and Jacobson.[2]

*Table LXXV.—Potassium Nickel Sulphate, 25° (Jones and Caldwell)*

| *V* | $K_2SO_4$ | $NiSO_4$ | Sum | $K_2Ni(SO_4)_2$ | Diff. | Diff. Per cent. |
|---|---|---|---|---|---|---|
| 8 | 182.4 | 77.9 | 260.3 | 219.5 | —40.8 | —15.6 |
| 40 | 220.3 | 109.0 | 329.3 | 291.6 | —37.7 | —11.4 |
| 80 | 237.9 | 122.8 | 360.7 | 323.7 | —37.0 | —10.3 |
| 400 | 262.2 | 173.1 | 435.3 | 400.2 | —35.1 | — 8.0 |
| 800 | 273.0 | 194.8 | 467.8 | 438.0 | —29.0 | — 6.2 |

*Table LXXVI.—Potassium Nickel Sulphate*

0°

| *V* | $K_2SO_4$ | $NiSO_4$ | Sum | $K_2Ni(SO_4)_2$ | Diff. | Diff. Per cent. |
|---|---|---|---|---|---|---|
| 8 | 101.9 | 40.4 | 142.3 | 122.6 | —19.7 | —13.8 |
| 32 | 117.9 | 54.8 | 172.7 | 155.4 | —17.3 | —10.0 |
| 128 | 131.9 | 73.9 | 205.8 | 187.5 | —18.3 | — 8.9 |
| 512 | 142.7 | 93.1 | 235.8 | 219.6 | —16.2 | — 6.9 |
| 1024 | 145.0 | 100.4 | 245.4 | 235.5 | — 9.9 | — 4.0 |
| | | | 35° | | | |
| 8 | 219.8 | 90.9 | 310.7 | 268.3 | —42.4 | —13.7 |
| 32 | 256.9 | 123.0 | 379.9 | 339.7 | —40.2 | —10.6 |
| 128 | 291.0 | 168.4 | 459.4 | 414.1 | —45.3 | — 9.8 |
| 512 | 318.4 | 213.5 | 531.9 | 490.7 | —41.2 | — 7.7 |
| 1024 | 325.0 | 234.6 | 559.6 | 527.1 | —32.5 | — 5.8 |

The percentage "differences" at 0° and 35° agree closely with those found by Jones and Caldwell at 25°, showing that the relations which they established as holding at 25° are also true at higher and lower temperatures. Our results also accord with the general law that dissociation is nearly independent of temperature.

---

[1] This Journal, **25**, 349 (1901).

[2] *Ibid.*, **40**, 390 (1908).

## SUMMARY

1. The molecular conductivities of fifteen inorganic salts from 0° to 35°, and of sixteen inorganic salts from 35° to 65°, were measured by the Kohlrausch method. The temperature coefficients of conductivity, both in conductivity units and in percentages, were calculated for these salts through the ranges of temperature above stated. The percentage dissociations were also calculated in all cases where the data were sufficient.

2. Jones and his coworkers[1] have shown that the ions of an electrolyte are hydrated in aqueous solutions, and that the complexes break down with rise in temperature, thus increasing the conductivity. If this is true, substances of large hydrating power should have large temperature coefficients of conductivity. Jones[2] showed this to be true for the substances studied by Jones and West.[3] The substances which we have studied show the same relations and our results are in perfect accord with the theory of hydration.

3. Hydrolysis is evidently a frequent cause of abnormally great conductivity. It is increased both by dilution and by rise in temperature.

4. Another probable cause of abnormally rapid increase in conductivity is decrease in polymerization. There is evidence that sulphates are polymerized in concentrated solutions.

5. Observers have found an increase in the conductivity of a solution of a chromium salt when it is changed from the violet to the green variety. Our results show that while the conductivity is increased in concentrated solutions by this change, the increase is relatively less at higher dilutions. The conductivity of the green variety may even fall below that of the violet variety. This would appear to show that the green variety is not as susceptible to hydrolysis by dilution as is the normal violet form.

---

[1] Hydates in Aqueous Solution; Carnegie Institution of Washington, Publication No. **60**.

[2] This Journal, **35**, 445 (1906).

[3] *Ibid.*, **34**, 357 (1905).

6. Jones and his coworkers[1] found that the conductivities of alums and other double salts were less than the sum of the conductivities of the constituent salts. They inferred that double salts exist as such to some extent in concentrated solutions. Their work was done at 25°. We have made similar comparisons at other temperatures, and find that the relations pointed out by them as holding at 25° also manifest themselves from 0° to 65°. In addition, our results show that the breaking down or dissociation of double salts, like dissociation in general, is little affected by temperature.

The following general relations, established by previous investigators, are true of the salts which we have studied:

7. The temperature-conductivity curves for concentrated solutions are nearly straight lines; at higher dilutions the curves are often parabolic.

8. The percentage temperature coefficients increase with dilution, but decrease with temperature. Temperature coefficients in conductivity units increase with dilution.

9. Dissociation decreases with temperature. Four salts among those studied seem to be exceptions to the rule.

Work along the above lines will be extended to all of the more common electrolytes, organic and inorganic.

JOHNS HOPKINS UNIVERSITY
May, 1911

---

# THE VISCOSITY AND FLUIDITY OF SUSPENSIONS OF FINELY-DIVIDED SOLIDS IN LIQUIDS

BY EUGENE C. BINGHAM AND T. C. DURHAM

[TWELFTH COMMUNICATION BEARING ON THIS SUBJECT]

It was pointed out in a recent paper[2] that there is very little literature upon the subject of the viscosity of suspensions. It has long been observed that dust must be carefully excluded from liquids whose viscosities are to be measured by the method of Poiseuille. Among more recent workers may be mentioned Thorpe and Rodger,[1] who took great pains in this matter. On the other hand, Friedländer[2] noted that suspensions of rosin in water which were highly opalescent affected the viscosity scarely any. Bose[3] notes that a suspension of finely divided quartz particles in a mixture of bromoform and water resembles an emulsion, but that the viscosity of the mixture, when dilute, is but little greater than that of the bromoform and water mixture alone. The apparent contradiction is probably explained by the fact that dust is composed partly of lint which is of such large dimensions that it is unable to pass through the capillary and hence forms an obstruction at the entrance to the latter. On the other hand, the particles of rosin in the second case must be exceedingly small, for we have observed that they remain suspended even after standing for months at room temperature. But the concentration of the suspension investigated by Friedländer was very small, being less than one-tenth of one per cent. That the presence of a solid, whose fluidity must be regarded as practically zero, should not lower the fluidity of a liquid in which it might happen to be suspended, even although the concentration might be small, seemed so very remarkable that it appeared worth while to make it the subject of special study. Especially is this true since only with a knowledge of these effects can a theory of paints and lubricants be established. The work of Schwedoff[4] on the rigidity of liquids may be referred to in this connection.

---

[1] Jones and Mackay: THIS JOURNAL, **19**, 83 (1897). Jones and Ota: *Ibid.*, **22**, 5 (1899). Jones and Knight: *Ibid.*, **22**, 110 (1899). Jones and Caldwell: *Ibid.*, **25**, 349 (1901).

[2] Bingham and White: J. Am. Chem. Soc., **33**, 1257 (1911).

As materials for study, it seemed desirable to use substances which could be obtained in a very finely divided condition; but the materials must be insoluble in the liquids employed, so as to avoid the complications which would arise if partial solution took place. It was, of course, desirable to select substances which would stay in suspension for a considerable time, hence large differences in specific gravity between the liquid and solid were undesirable. The rate of settling, however, is by no means dependent solely upon the difference in specific gravities, or upon the fineness of subdivision of the solid, but it is dependent very largely upon circumstances which would at first seem to be quite extraneous. These conditions will be discussed later.

---

[1] Phil. Trans., **185**, A. 411, 414, 415, 444 (1894).

[2] Z. physik. Chem., **38**, 430 (1901).

[3] Physik. Z., **8**, 347 (1907).

[4] Rapport au Congrès de Physique, **1**, 478 (1900).

The Richmond deposits of infusorial earth are composed principally of silica and the material is very light. When mixed with a considerable quantity of distilled water, a portion of the material will remain in suspension for a very long time, not becoming clear after several weeks. It was observed that tap water or distilled water containing a very little salt, such as sodium, potassium, or ammonium chlorides, would cause this suspension to coagulate and settle rapidly. A considerable amount of material was elutriated, the portion remaining in suspension after fifteen minutes being siphoned off and evaporated to dryness. This material was pulverized and bolted through a 200-mesh sieve and preserved in the dry condition. The material was cream-colored. It darkened somewhat on heating to a high temperature, presumably due to the presence of organic matter.

A supply of the finest English china clay was obtained from the Chesapeake Pottery Co., of Baltimore. On drying, the material nearly all passed through a 200-mesh sieve, without other preliminary treatment. It seemed impossible to elutriate the material satisfactorily by suspending it in pure water, as it coagulated and settled *en masse*. But it was noticed that the effect of potassium chloride and ammonium chloride on the clay suspension was exactly the opposite of that on the infusorial earth, the coagulation being much less marked.

The graphite sold under the name of "Aquadag" for lubrication was obtained from the International Acheson Graphite Company, of Niagara Falls, N. Y. It is a suspension in water which does not settle and hence is suitable for our purposes.

As media for the suspensions, water and alcohol seemed to be the most suitable liquids for our present purposes. The water was redistilled from both chromic acid and barium hydroxide and was quite dust-free. The alcohol was dehy-

ol. 46
1911

drated with lime, distilled, and, after adding a little metallic sodium, redistilled through a Glinsky distilling head.

It seemed unwise to attempt to use the apparatus referred to in a recent paper, after the method of Poiseuille. With a capillary tube of about one-tenth mm. diameter there would be danger of permanently plugging the tube. A tube of larger bore could be used if it were sufficiently long and the pressure not too high. The Ostwald type of viscometer semed best suited for our present purposes on account of its extreme simplicity, but it was observed by one of us several years ago that when this type of viscometer was calibrated with one liquid it would not give perfectly satisfactory values for the viscosities of other liquids whose viscosities are known. The same thing has been noted by other workers, among whom we may cite Alexander Findlay. Nevertheless viscosities can now be measured with great accuracy, as has been abundantly proved by the work of Thorpe and Rodger and others. Although we could not hope to attain such a high degree of accuracy with the solid suspensions, it seemed worth while to make a study of the use of the Ostwald viscometer.

An imported viscometer was tested with water, alcohol, and ether over a series of temperatures. Care was taken to have the capillary uniformly vertical, and the temperature of the bath was kept constant to within a tenth of a degree. Impurities were carefully excluded from the apparatus. The time was recorded with a high grade stop-watch which was tested for its reliability. The results are given in the following tables:

*Table I—The Viscosity of Water as Measured by Mr. Adrian Thomas with the Ostwald Viscometer "A"*

| Temp. | Time in seconds Average | Viscosity | Values by other observers | Percentage difference |
|---|---|---|---|---|
| 10.0 | 79.2 | 0.01303 | 0.01307 | —0.30 |
| 15.0 | 69.2 | 0.01134 | 0.01140 | —0.52 |
| 25.0 | 55.0 | Standard | 0.00895 | .... |
| 30.0 | 49.2 | 0.00804 | 0.00801 | +0.37 |
| 36.0 | 44.2 | 0.00727 | 0.00706 | +2.08 |
| 40.0 | 40.9 | 0.00667 | 0.00655 | +1.79 |
| 45.0 | 37.8 | 0.00613 | 0.00599 | +2.44 |
| 50.0 | 35.0 | 0.00567 | 0.00551 | +2.64 |

In this and the following tables, the time given is the average of two or more observations.

*Table II—The Viscosity of Ethyl Alcohol as Measured by Mr. Adrian Thomas with the Ostwald Viscometer "A"*

| Temp. | Time in seconds Average | Viscosity | Viscosity by other observers | Percentage difference |
|---|---|---|---|---|
| 8.0 | 115.5 | 0.01515 | 0.01513 | +0.1 |
| 9.0 | 112.3 | 0.01470 | 0.01481 | —0.74 |
| 10.0 | 110.3 | 0.01442 | 0.01449 | —0.49 |
| 15.0 | 100.8 | 0.01310 | 0.01320 | —0.76 |
| 20.0 | 92.0 | 0.01191 | 0.01192 | —0.09 |
| 25.0 | 84.2 | 0.01085 | 0.01091 | —0.55 |
| 35.0 | 71.1 | 0.00904 | 0.00908 | —0.53 |
| 45.0 | 60.2 | 0.00758 | 0.00762 | —0.61 |

*Table III—The Viscosity of Ethyl Ether as Measured by Mr. Adrian Thomas with the Ostwald Viscometer "A"*

| Temp. | Time in seconds Average | Viscosity | Viscosity by other observers | Percentage difference |
|---|---|---|---|---|
| 8.0 | 24.9 | 0.003002 | 0.002640 | +16.0 |
| 10.0 | 24.5 | 0.002915 | 0.002585 | +10.0 |
| 15.0 | 23.8 | 0.002804 | 0.002465 | +13.0 |
| 20.0 | 23.5 | 0.002751 | 0.002345 | +16.0 |
| 25.0 | 22.5 | 0.002613 | 0.002232 | +12.0 |
| 30.0 | 21.8 | 0.002519 | 0.002120 | +16.0 |

We are indebted to Mr. Adrian Thomas for these measurements but quite similar results have been obtained by one of the authors of this paper, working with this type of viscometer.

From the above tables it is clear that the results are not satisfactory. It may be properly objected that the viscometer used was unsuited to the measurement of the viscosity of ether, but it must be noted that the deviations for water are of the same kind, although not so great. In other words, the deviations here shown are characteristic of this form of viscometer. The time of flow is too small, in all of the measurements, for accurate work, since the time can be estimated only to two-tenths of a second. In the case of ether it is possible that the velocity of the liquid in the capillary was so great that the motion became turbulent, instead of linear, as should be the case. But by far the greatest source of error with this form of apparatus arises from the fact that no correction is made for the kinetic energy imparted to the liquid on entering the capillary. That this correction is indeed adequate to explain the discrepancies observed may be inferred from the formula used by Thorpe and Rodger in calculating absolute viscosities,

$$\eta = \pi r^4 tp / 8lv - \rho v / 8\pi lt$$

where $r$ is the radius of the capillary, $t$ the time of flow, $p$ the difference of pressure in dynes per sq. cm., $l$ the length of the capillary, $v$ the volume of liquid passing through the tube and $\rho$ the density of the liquid. The second term is the correction term for kinetic energy. In the apparatus in question the volume of liquid is about four cc. and the length of the capillary is about seven cm. This gives a correction of 0.007, which is more than sufficient, but we must recall that no correction was included when the instrument was standardized.

An attempt was now made to construct an apparatus with which the correction might be reduced to much smaller dimensions by using a longer and smaller capillary. The volume of liquid used in the Ostwald viscometer, 4 cc., is larger than is necessary since, if the volume can be read to one one-thousandth cc., an accuracy of one-tenth of one per cent. can be obtained with only one cc. of liquid. Thus the time of flow can be reduced.

In the new apparatus "B" made by Mr. Adrian Thomas, the volume of liquid was 2.3 cc. and the length of the capillary 18.4 cm. The results obtained are given in the following tables:

*Table IV—The Viscosity of Water as Measured by Mr. Adrian Thomas with Viscometer "B"*

| Temp. | Time in seconds Average | Viscosity | Viscosity by other observers | Percentage difference |
|---|---|---|---|---|
| 25.0 | 630.4 | 0.00892 | 0.00895 | —0.3 |
| 30.0 | 565.4 | 0.00802 | 0.00801 | +0.1 |
| 35.0 | 509.1 | 0.00724 | 0.00725 | —0.1 |
| 40.0 | 462.5 | 0.00657 | 0.00655 | +0.3 |
| 45.0 | 424.3 | 0.00601 | 0.00599 | +0.3 |
| 50.0 | 391.5 | 0.00553 | 0.00551 | +0.3 |
| 55.0 | 360.1 | 0.00506 | 0.00508 | —0.2 |
| 60.0 | 334.1 | 0.00468 | 0.00470 | —0.2 |
| 65.0 | 311.4 | 0.00435 | 0.00437 | —0.2 |
| 70.0 | 291.3 | 0.00406 | 0.00407 | —0.2 |
| 75.0 | 274.0 | 0.00381 | 0.00381 | 0.0 |
| 80.0 | 258.2 | 0.00358 | 0.00357 | +0.3 |
| 85.0 | 242.8 | 0.00335 | 0.00336 | —0.3 |
| 90.0 | 230.4 | 0.00317 | 0.00317 | 0.0 |
| 95.0 | 219.0 | 0.00300 | 0.00300 | 0.0 |

*Table V—The Viscosity of Ethyl Ether as Measured by Mr. Adrian Thomas with Viscometer "B"*

| Temp. | Time in seconds Average | Viscosity | Viscosity by other observers | Percentage difference |
|---|---|---|---|---|
| 1.7 | 278.6 | 0.00291 | 0.00284 | +2.1 |
| 2.0 | 276.8 | 0.00290 | 0.00281 | +3.1 |
| 5.0 | 269.1 | 0.00280 | 0.00272 | +2.5 |
| 10.0 | 257.6 | 0.00266 | 0.00259 | +2.6 |
| 15.0 | 246.5 | 0.00253 | 0.00246 | +1.0 |
| 20.0 | 236.0 | 0.00240 | 0.00234 | +2.2 |
| 25.0 | 227.0 | 0.00229 | 0.00223 | +2.1 |
| 30.0 | 217.6 | 0.00219 | 0.00212 | +2.8 |

The agreement is very much better with this viscometer, being satisfactory in the case of water.

Another viscometer was then made for use in measuring the viscosities of solid suspensions, a capillary of larger diameter than the above but of considerably greater length, 40.8 cm., being used. The values for the instrument with pure liquids are as follows:

*Table VI—The Fluidity of Water at Different Temperatures, as Measured with Viscometer "C"*

| Temp. | Time in seconds Average | Fluidity | Fluidity observed by Thorpe and Rodger | Percentage difference |
|---|---|---|---|---|
| 30.0 | 225.8 | 125.8 | 125.4 | +0.3 |
| 35.0 | 204.0 | 139.5 | 138.9 | +0.4 |
| 40.0 | 185.4 | 153.8 | 153.0 | +0.5 |
| 45.0 | 170.0 | 168.0 | 167.4 | +0.4 |
| 50.0 | 156.6 | 182.9 | 182.4 | +0.3 |
| 55.0 | 145.2 | 197.7 | 197.8 | 0.0 |
| 60.0 | 134.9 | 213.1 | 213.3 | 0.0 |
| 65.0 | 125.9 | 229.1 | 229.5 | —0.1 |
| 70.0 | 117.8 | 245.6 | 246.3 | —0.2 |
| 75.0 | 110.9 | 261.7 | 263.5 | —0.7 |
| 80.0 | 104.4 | 278.7 | 280.5 | —0.6 |
| 85.0 | 99.1 | 294.6 | 298.3 | —1.2 |
| 90.0 | 94.0 | 311.7 | 316.8 | —1.6 |

*Table VII—The Fluidity of Phenol at Different Temperatures, as Measured with Viscometer "C"*

| Temp. | Time in seconds Average | Fluidity | Fluidity observed by Bingham and White | Percentage difference |
|---|---|---|---|---|
| 45.0 | 1080.4 | 24.93 | 25.02 | —0.4 |
| 50.0 | 925.2 | 29.22 | 29.23 | 0.0 |
| 55.0 | 797.6 | 34.01 | 34.03 | 0.0 |
| 60.0 | 696.5 | 39.12 | 39.01 | —0.2 |
| 65.0 | 616.2 | 44.40 | 44.44 | 0.0 |
| 70.0 | 548.7 | 50.10 | 50.10 | 0.0 |
| 75.0 | 492.0 | 56.11 | 56.20 | —0.2 |
| 80.0 | 443.1 | 62.63 | 62.43 | +0.3 |
| 85.0 | 403.0 | 69.17 | 69.64 | —0.6 |
| 90.0 | 370.0 | 75.71 | 76.70 | —1.3 |

The volume of liquid in viscometer "C" was 8.15 cc. When we note that this large volume, in the case of water at high temperatures, flowed through the capillary in less than 100 seconds, we are not surprised that the agreement is unsatisfactory. The agreement at the lower temperatures seemed sufficient for the preliminary investigation at hand, where it was entirely uncertain what conditions would arise. It was, however, certain that the fluidities to be measured would be no greater than those of water. When measuring the viscosity of suspensions it was advantageous to use a comparatively large volume in order to minimize the error due to the liquid not draining properly.

The suspensions were made up by weight and the volumes calculated therefrom. The percentages in the following tables are expressed in terms of volume of solid to volume of mixture, on the supposition that the volume of the mixture is the sum of the volumes of each of the components singly. The specific gravities were taken from the tables of Landolt, Börnstein and Meyerhoffer.

The viscometer was kept at a constant temperature in a water bath which was vigorously stirred, the temperature being read on a thermometer divided to one one-hundredths of a degree and calibrated at the German Reichsanstalt. The volume of the liquid in the viscometer was kept constant by causing any excess to overflow the viscometer before the measurement began. A mark was etched on the lower part of the instrument to indicate the exact volume necessary. Complete mixing of the liquid was insured by blowing air through the mixture. By using air which was pure except for the vapor of the liquid in the viscometer, appreciable error from evaporation was avoided.

*Table VIII—The Fluidity of an Approximately 3.1 Per Cent. Suspension of Infusorial Earth in Water*

| Temp. | Volume per cent solid | Time | Fluidity Viscometer "C" | Fluidity Viscometer "B" |
|---|---|---|---|---|
| 25.0 | 3.18 | 309.3 | 87.79 | |
| 30.0 | 3.17 | 281.5 | 97.5 | 97.7 |
| 35.0 | 3.17 | 257.0 | 106.8 | 107.2 |
| 40.0 | 3.16 | 234.4 | 117.3 | ... |
| 45.0 | 3.15 | 215.8 | 127.6 | 128.8 |
| 50.0 | 3.14 | 199.4 | 138.3 | ... |
| 55.0 | 3.14 | 186.0 | 148.5 | 150.9 |
| 60.0 | 3.13 | 172.9 | 160.1 | ... |
| 65.0 | 3.12 | 163.2 | 169.9 | 177.4 |
| 70.0 | 3.12 | 153.6 | 180.8 | ... |
| 75.0 | 3.11 | 143.5 | 193.7 | ... |

*Table IX—The Fluidity of an Approximately 6.4 Per Cent. Suspension of Infusorial Earth in Water as Measured with Viscometer "C"*

| Temp. | Volume per cent. of solid | Time | Fluidity |
|---|---|---|---|
| 30.0 | 6.46 | 421.5 | 62.1 |
| 35.0 | 6.44 | 384.2 | 69.0 |
| 45.0 | 6.41 | 325.5 | 81.1 |
| 55.0 | 6.39 | 280.0 | 94.8 |
| 65.0 | 6.37 | 246.0 | 109.0 |

*Table X—The Fluidity of an Approximately 9.3 Per Cent. Suspension of Infusorial Earth in Water as Measured with Viscometer "C"*

| Temp. | Volume per cent. of solid | Time | Fluidity |
|---|---|---|---|
| 25.0 | 9.37 | 760.0 | 34.08 |
| 30.0 | 9.36 | 703.7 | 36.3 |
| 35.0 | 9.34 | 662.8 | 38.7 |
| 45.0 | 9.30 | 588.9 | 43.8 |
| 55.0 | 9.27 | 492.0 | 52.6 |
| 65.0 | 9.23 | 458.0 | 56.7 |
| 75.0 | 9.19 | 442.5 | 58.9 |

*Table XI—The Fluidity of an Approximately 11.6 Per Cent. Suspension of Infusorial Earth in Water Measured with Viscometer "C"*

| Temp. | Volume per cent. of solid | Time | Fluidity |
|---|---|---|---|
| 30.0 | 11.63 | 1702.8 | 14.7 |
| 35.0 | 11.59 | 1525.0 | 17.0 |
| 65.0 | 11.48 | 1440.0 | 17.2 |

Grouping the fluidities together and including the values of the fluidity of pure water given by Thorpe and Rodger, we have:

*Table XII—The Fluidities of Suspensions of Infusorial Earth in Water at Different Temperatures and Concentrations*

| | Approx. per cent. earth by volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 0.9 | 3.1 | 6.4 | 9.3 | 11.6 |
| | Per cent. earth by weight | | | | | |
| | 0 | 1.96 | 6.75 | 13.24 | 18.57 | 22.53 |
| Temp. | Fluidity | Fluidity | Fluidity | Fluidity | Fluidity | Fluidity |
| 25.0 | 112.0 | ... | 87.8 | .... | 34.1 | .... |
| 30.0 | 125.4 | 117.7 | 97.5 | 62.1 | 36.3 | 14.7 |
| 35.0 | 138.9 | ... | 106.8 | 69.0 | 38.7 | 16.4 |
| 40.0 | 153.0 | ... | 117.3 | .... | .... | .... |
| 45.0 | 167.4 | ... | 127.6 | 81.1 | 43.8 | 17.0 |
| 50.0 | 182.4 | ... | 138.3 | .... | .... | .... |
| 55.0 | 197.8 | ... | 148.5 | 94.8 | 52.6 | .... |
| 60.0 | 213.3 | ... | 160.1 | .... | ... | .... |
| 65.0 | 229.5 | ... | 169.9 | 109.0 | 56.7 | 17.2 |
| 70.0 | 246.3 | ... | 180.8 | .... | .... | .... |
| 75.0 | 263.5 | ... | 193.7 | .... | 58.9 | .... |

*Table XIII—The Fluidities of Suspensions of English China Clay in Water at Different Temperatures and Concentrations as Measured with Viscometer "C"*

| Temp. | Weight per cent. of clay | Volume per cent. of clay | Time | Fluidity |
|---|---|---|---|---|
| 30.0 | 2.15 | 0.580 | 259.7 | 104.0 |
| 35.0 | .. | 0.576 | 239.4 | 113.8 |
| 40.0 | .. | 0.573 | 213.6 | 128.3 |
| 50.0 | .. | 0.566 | 181.5 | 152.7 |
| 65.0 | .. | 0.558 | 147.9 | 190.6 |
| 30.0 | 5.45 | 1.468 | 327.7 | 51.2 |
| 35.0 | .. | 1.465 | 298.5 | 90.9 |
| 45.0 | .. | 1.458 | 248.0 | 109.9 |
| 55.0 | .. | 1.452 | 216.8 | 126.2 |
| 65.0 | .. | 1.446 | 189.1 | 145.3 |
| 30.0 | 9.45 | 2.630 | 630.1 | 41.5 |
| 30.0 | 16.28 | 4.794 | 1794.8 | 13.76 |

*Table XIV—The Fluidities of Suspensions of Infusorial Earth in Ethyl Alcohol at Different Temperatures and Concentrations, as Measured with Viscometer "C," and the Fluidity of Pure Alcohol by Thorpe and Rodger*

| Temp. | Weight per cent. of earth | Volume per cent. of earth | Time | Fluidity |
|---|---|---|---|---|
| 30.0 | 3.00 | 1.082 | 376.4 | 94.1 |
| 35.0 | .. | 1.075 | 344.7 | 103.4 |
| 45.0 | .. | 1.062 | 296.2 | 121.9 |
| 55.0 | .. | 1.048 | 254.1 | 144.0 |
| 65.0 | .. | 1.034 | 220.0 | 168.5 |
| 30.0 | 15.82 | 6.237 | 667.8 | 48.6 |
| 35.0 | ... | 6.200 | 594.8 | 54.9 |
| 45.0 | ... | 6.121 | 544.4 | 60.7 |
| 55.0 | ... | 6.045 | 501.2 | 66.7 |
| 30.0 | 0.0 | 0.0 | | 101.0 |
| 40.0 | .. | 0.0 | | 120.7 |
| 50.0 | .. | 0.0 | | 143.7 |
| 60.0 | .. | 0.0 | | 169.4 |
| 70.0 | .. | 0.0 | | 198.3 |

*Table XV—The Fluidities of Suspensions of Graphite in Water at Different Temperatures and Concentrations as Measured with Viscometer "C"*

| Temp. | Volume per cent. of graphite | Weight per cent. of graphite | Time | Fluidity |
|---|---|---|---|---|
| 30.0 | 0.396 | 0.852 | 242.6 | 116.8 |
| 35.0 | 0.395 | .. | 218.4 | 129.8 |
| 45.0 | 0.394 | .. | 182.3 | 156.3 |
| 55.0 | 0.392 | .. | 154.8 | 184.9 |
| 65.0 | 0.390 | .. | 133.3 | 215.5 |
| 30.0 | 1.048 | 2.236 | 278.4 | 100.9 |
| 35.0 | 1.046 | . | 250.8 | 113.4 |
| 45.0 | 1.042 | .. | 209.8 | 135.0 |
| 55.0 | 1.037 | .. | 174.4 | 161.7 |
| 65.0 | 1.032 | .. | 148.4 | 192.1 |

The results are shown graphically in Figs. I–IV. It was to be expected that any relation would be most easily observed by plotting the results in terms of volume percentages. The results show that the relations are extremely simple. It

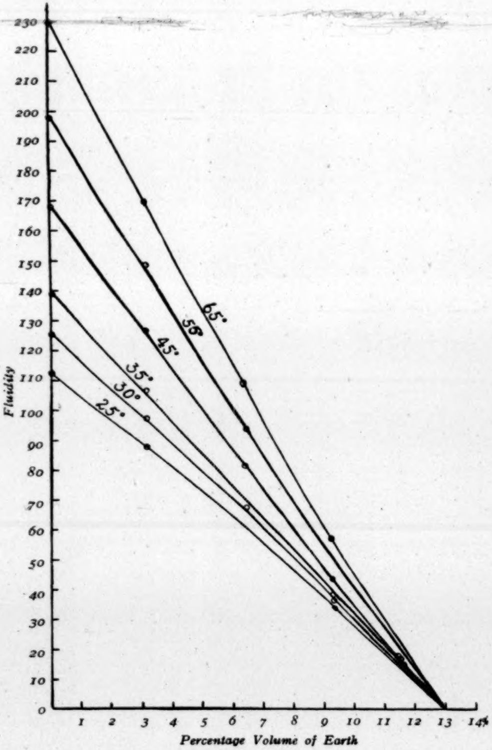


Fig. I—The Fluidity of Suspensions of Infusorial Earth in Water at Different Temperatures and Concentrations

is evident that finely divided substances in suspension depress the fluidity of the liquids in which they are suspended by amounts which are directly proportional to the volume of the solid. But the depression is such that a zero value of fluidity is reached at a definite but comparatively small percentage, by volume, of the solid. This composition where the fluidity becomes zero is the same for all temperatures, as all of the diagrams indicate. When we note that the temperature coefficient of fluidity of an oil is very great but that a suspension of the critical concentration has a zero temperature coefficient, it becomes evident that a mixture like "aquadag" has a great advantage as a lubricant where there are consid-

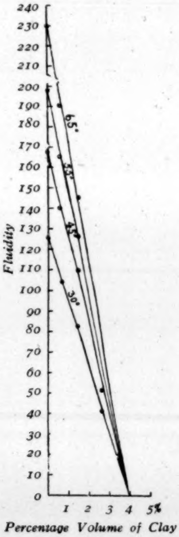


Fig. II—The Fluidity of Suspensions of China Clay in Water at Different Temperatures and Concentrations

erable temperature fluctuations. Furthermore, the zero of fluidity is apparently not dependent upon the particular apparatus used, as is indicated by Table VIII, where it is shown that two different viscometers give duplicating values. This composition seems to demarcate viscous from plastic flow. This is apparently the first time that the limits of viscous flow and plastic flow have been sharply differentiated, although Maxwell clearly defined them. This is probably to be accounted for by the fact that the viscosity curve is not a simple curve, whose meaning is immediately apparent. It is to be noted that the mixture having zero fluidity is not stiff, as might be supposed; it will not even maintain its own shape in the containing bottle. But it is difficult to work with mixtures which even approach this critical composition, for they drain very badly. A portion of the mixture evidently reaches the critical composition and sticks to the walls of the viscometer and does not flow, as would a viscous liquid.

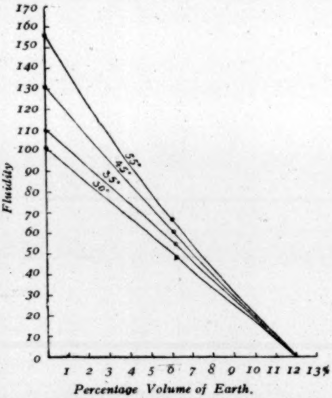


**Fig. III—The Fluidity of Suspensions of Infusorial Earth in Ethyl Alcohol at Different Temperatures and Concentrations**

That the law enunciated above, that the lowering of the fluidity is proportional to the percentage by volume of the suspended solid, is true as a first approximation may be proved by calculating the fluidity of a 1.04 per cent. suspension of graphite in water, from the known fluidity of water and the experimentally determined fact that a 5.5 per cent. mixture has a zero fluidity, by means of the formula $\varphi_s = \left(1 - \frac{c}{K}\right)\varphi_\omega$, where $c$ is the volume concentration of the unknown suspension, $K$ the volume concentration of the suspension of zero fluidity, and $\varphi_\omega$ is the fluidity of the pure solvent at the given

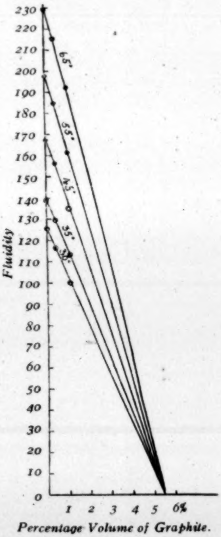


**Fig. IV—The Fluidity of Suspensions of Graphite-Aquadag in Water at Different Temperatures and Concentrations**

temperature. The observed and calculated values are given in the following table:

*Table XVI—Calculation of the Fluidity of Graphite Suspensions on the Assumption that a 5.5 Per Cent. Suspension has Zero Fluidity*

| Temp. | Volume per cent. | Fluidity observed | Fluidity calculated |
|---|---|---|---|
| 30.0 | 1.048 | 100.9 | 101.9 |
| 35.0 | 1.046 | 113.4 | 112.4 |
| 45.0 | 1.042 | 135.0 | 135.8 |
| 55.0 | 1.032 | 161.7 | 160.5 |
| 65.0 | 1.032 | 192.1 | 186.3 |

In viscous flow we must think of the flow as being in the liquid *between* the solid particles, the particles of solid in no way contributing to that flow. The results given above show that not only is this true, but it is evident that the particles of solid are able to extend their influence somewhat beyond the actual space which they fill as a compact solid. Thus, in a mixture of zero fluidity it seems probable that the particles of solid are able to exert their forces of cohesion throughout the whole mass of liquid. When the spheres of action thus fill the whole space, there is no longer opportunity for true viscous flow.

As to the size of the individual particles, we seem forced to the conclusion that the zero of fluidity is not primarily dependent upon the size of the particles of the solid in the dry condition. The particles of clay, and particularly the particles of graphite, were very small and we might suppose that the fluidity would be correspondingly high; however, it was much lower than for the infusorial earth whose particles were rather coarse. A reason for this behavior may be inferred from the fact that mixtures of clay in water coagulate readily, so that the particles are really of large dimensions. Moreover, we have observed that the amount of coagulation and the fluidity are greatly affected by small amounts of impurities.

Dr. Acheson has shown that various substances, as tannin and extract of straw, will promote the suspension of graphite, while acids will coagulate it. So far as is known to the authors, no one has related viscosity to these phenomena; yet, as shown in a recent paper, anything which causes a mixture to separate out will decrease its fluidity. That viscosity measurements afford a delicate means of detecting these changes is indicated by the following table:

*Table XVII—The Effect of Adding Small Amounts of Substances to Suspensions at 30° .0*

| Per cent. solid | Fluidity | Substance added | Resultant fluidity |
|---|---|---|---|
| 3.17 infus. earth | 97.5 | 0.03 gram KCl | 83.6[1] |
| 6.46 infus. earth | 62.1 | 0.01 gram KCl | 53.2[2] |
| 9.36 infus. earth | 36.3 | 0.05 gram KCl | 22.7 |
| 0.58 clay | 104.0 | 0.02 gram KCl | 106.5 |
| 2.63 clay | 41.5 | 0.02 gram KCl | 65.8 |
| 0.396 graphite | 116.8 | 0.02 gram KCl | 116.9 |
| 0.396 graphite | 116.8 | 1 drop 90 per cent. acetic acid | 64.5[3] |

As to the cause of these extraordinary effects, there appears to be no easy explanation. The table shows that the effect cannot be due to the fluidity of the added substance. If the coagulation were due merely to the presence of an electrolyte, then acids and bases would not act in opposite manner. Furthermore, potassium chloride would not act in exactly opposite manners upon infusorial earth and clay, coagulating the formed and delaying the coagulation of the latter. An instructive analogy may be obtained from the behavior of a suspension of colophony in water, made by dissolving the colophony in alcohol and adding this to water. On exposing it to the air the alcohol may be evaporated off. This suspension is like the permanent suspension of infusorial earth in that it will remain permanently suspended. Like it, too, it may be coagulated by acids. On the addition of alkalis the coagulation is destroyed. This action is so easily observed and so sharply defined that it may be used to test

[1] Two grams more of potassium chloride raised the fluidity to 86.5.

[2] Three-hundredths gram of potassium hydroxide raised the fluidity to 58.3 at first but the value then steadily fell, presumably due to the action of the alkali upon the clay. On adding hydrochloric acid the fluidity fell greatly.

[3] Alkali nearly restored the fluidity to its former value.

for hydrogen or hydroxyl ions, one drop of half-normal acid or base giving a very decided change at the neutral point in 50 to 100 cc. of liquid. The explanation in this case is evident. The particles of the acid anhydride, being insoluble in water, adhere together, resulting in coagulation. As soon as an alkali is added there is formed the salt of the acid, which is soluble in water, so that the particles no longer adhere, a layer of the salt or soap surrounding each particle. The action of acids and alkalis here described is quite general, but whether the explanation of the above case can be extended to explain the suspension of such chemically inert substances as graphite, clay, infusorial earth, rouge, etc., seems rather far-fetched. Of course, a thin layer of a resinous substance on the surface of the particles would be all that would be necessary.

We have tried several colloids, as gelatin, agar-agar and arsenious sulphide, and found that they do aid suspension when in the right proportions. A suspension of colophony in water does not exert much action upon the suspension of other solids, but the effect of a rosin soap made by adding an alkali to the suspension of colophony is very marked. Other alkaline substances, like sodium oleate, sodium carbonate and dilute ammonia, greatly promote suspension. A weak acid like boric acid is not pronounced in its influence, while strong acids and acid salts like sodium acid sulphate produce immediate coagulation.

From the above, it is evident that the zero of fluidity can be changed by the presence of small amounts of impurities. It would be therefore unwarranted to connect the value of this composition with the specific nature of the substance. It is to be noted in this connection that graphite requires many times as much water or oil to make it into a paste as is required for a substance like white lead. We have made measurements to show that the composition corresponding to the zero of fluidity is considerably higher for the white lead than for the graphite. Whether there is a simple relation between the composition corresponding to zero fluidity and the amount of liquid necessary to make a paste of a given consistency we are not prepared to state. It would seem to be necessary to first study the nature of plastic flow. That the two viscometers "B" and "C" gave fairly duplicating results, even though the hydrostatic pressures were somewhat different, does not prove conclusively that the zero of fluidity is independent of the pressure. Further work will be devoted to these points.

## CONCLUSIONS

1. The viscosity of dilute suspensions can be easily measured by the capillary-tube method. The fluidity decreases rapidly as the volume concentration of the solid increases.

2. The decrease in the fluidity is directly proportional to the volume concentration of the solid.

3. At a definite concentration a zero fluidity is reached which apparently demarcates viscous from plastic flow.

4. This composition is independent of the temperature and of the dimensions of the particular apparatus employed in the viscosity measurements.

5. This composition is not the same for different substances suspended in the same liquid, nor is it necessarily the same for one substance suspended in different liquids.

6. The fluidity and the stability of suspensions are greatly altered by small amounts of impurities which appear to affect the cohesion between the particles. Foremost in their effects are hydrogen and hydroxyl ions. But their action is exactly opposite, for the former coagulate suspensions, while the latter promote them.

7. The much-used "Ostwald viscometer" is open to a serious defect from the theoretical point of view in that it fails to take into consideration the varying losses of kinetic energy. In practice, it has been found that the rate of transpiration must be very great in order to secure entirely satisfactory results.

Richmond College
Richmond, Va.

# THE RELATION OF HEAT OF VAPORIZATION TO OTHER CONSTANTS AT THE BOILING TEMPERATURE OF SOME LIQUIDS AT ATMOSPHERIC PRESSURE

BY JACK P. MONTGOMERY

Pictet[1] showed, by the application of the theory of heat to the study of volatile liquids, that at the boiling point, under fixed pressure, cohesion is constant, and that at the same temperature and pressure the latent heat of vaporization is inversely proportional to the molecular weight.

Trouton[2] observed that molecular heats of vaporization are directly proportional to the absolute temperature of the boiling point.

Schiff[3] determined a large number of heats of vaporization. He found that, in general, heat of vaporization decreases as the molecular weight increases, and increases as the absolute temperature of the boiling point. Neither of these relations alone could be formulated, but by combining the two a confirmation of Trouton's law was had. We have the formula

$$\frac{M\lambda}{T} = C$$

where $M$ is the molecular weight, $\lambda$ the heat of vaporization, and $T$ the boiling temperature on the absolute scale. Schiff found for a large number of substances 20.7 as average value for $C$.

Linebarger,[4] in discussing the above average found by Schiff, calls attention to the fact that the greatest divergences from this number are found in the case of water, the alcohols, and certain organic acids. Water and most of the alcohols are associated liquids, but in the state of vapor the molecules are simple, as is shown by the normal vapor density. When such liquids boil there occurs a dissociation of complex molecules into simple ones and this uses up heat in addition to that required for vaporization. Consequently these substances give a value for $C$ much higher than is expected. In the case of some organic acids, on the other hand, the liquid contains simple molecules while the vapor contains associated molecules. In such cases the value for $C$ is low. There are other organic acids which show association in both liquid and vapor and these also give widely varying results. Linebarger calls attention to the fact that the above classes of substances were omitted by Schiff in obtaining his average 20.7.

---

[1] Compt. rend., **82**, 260.

[2] Phil. Mag., **18**, 84.

[3] Ann. Chem. (Liebig), **234**, 343.

[4] Am. J. Sci., **49**, 380.

Dudley[1] has shown, in the case of certain esters of formic, acetic, propionic, butyric, and valeric acids, that the heat of vaporization, for each series of esters of the same acid, in a unit volume of vapor at a given temperature and pressure is proportional to the density and to the absolute boiling temperature. The same regularity is shown in the case of methyl, ethyl, propyl and butyl esters of given acids. In Dudley's paper the attempt is made to show that the acid radicals determine heat of vaporization in esters. From the heats of vaporization of certain esters he calculates that of the acids. But his conclusions are not in accord with later experimental evidence. Linebarger's observation that the heats of vaporization of organic acids are abnormal makes it impossible to calculate their vaporization constants.

Walden[2] has found that heat of vaporization is proportional to specific cohesion at the boiling temperature and that molecular cohesion is proportional to the absolute boiling temperature. These observations do not apply to substances undergoing association of molecules in the liquid or vapor.

In addition to those named, a large number of investigators have made contributions to the subject by the careful determination of various constants. The literature abounds in reports of the determination of heats of vaporization, boiling points, densities, etc., and a general acknowledgment must be made here.

It has been noted above that only those substances having simple molecules in both liquid and vapor are comparable when heat of vaporization is concerned. In this paper, giving some relations the writer has found to exist between heat of vaporization and some other constants, substances having associated moleclues in either liquid or vapor are, for the most part, purposely excluded.

---

[1] J. Am. Chem. Soc., **17**, 969.

[2] Z. physikal. Chem., **65**, 129.

1. With liquids at their respective boiling temperatures, under atmospheric pressure, the volume of a unit weight of vapor produced is directly proportional to the heat of vaporization. We have the equation

$$\frac{V-v}{\lambda} = C$$

when $V$ is the volume of 1 gram of vapor at the boiling temperature, $v$ the volume of 1 gram of the liquid at that temperature, and $\lambda$ the heat of vaporization.

In the following table the heats of vaporization are taken from the Landolt–Börnstein and the Castell-Evans tables. The volumes of the vapors were calculated from data derived from the same sources, correction being made for temperature and according to the equation of van der Waals. The volumes of the liquids were calculated from data given in various journals and books, correction being made for temperature where necessary.

| | $V-v$ | $\lambda$ | $C$ |
|---|---|---|---|
| Benzene | 369.5 | 93.5 | 3.952 |
| Ether | 333.6 | 86.0 | 3.879 |
| Carbon bisulphide | 337.6 | 86.7 | 3.894 |
| Ethyl acetate | 320.6 | 83.05 | 3.860 |
| Chloroform | 228.3 | 58.5 | 3.902 |
| Mercury | 240.5 | 62.0 | 3.879 |
| Carbon tetrachloride | 179.8 | 46.35 | 3.881 |
| Phosphorus trichloride | 206.6 | 52.0 | 3.98 |
| Ethylene oxide | 536.7 | 138.6 | 3.94 |
| Diethylamine | 368.9 | 91.0 | 3.94 |
| Ethylbenzene | 300.4 | 76.4 | 3.933 |
| Mesitylene | 281.3 | 71.75 | 3.92 |
| Cymene | 254.5 | 66.3 | 3.838 |
| Methyl iodide | 181.3 | 46.07 | 3.939 |
| Ethyl iodide | 180.5 | 46.87 | 3.851 |

The above substances were included in the table because they are representative of widely different classes, but the same relation was found for a large number of substances. The average of the values for $C$ in the above is 3.89. Esters of the fatty acids show a great degree of regularity, the value for $C$ being in most cases from 3.81 to 3.90.

Acetone, methylal, sulphur dioxide, tin tetrachloride and bromine give values for $C$ from 3.71 to 3.79. That is, a given quantity of heat does not produce as great a volume of vapor as would be expected from the above average. This is readily explained by the fact that those substances are slightly associated in the liquid state. Water and a number of the alcohols give values for $C$ lower than the average, ranging from 3.83 in the case of amyl alcohol to 2.95 for ethyl alcohol, the divergence of the values depending upon the degree of association in the liquid state.

The organic acids give varying values for $C$ from 3.56 to 5.68, these values being the complex result of the degree of association in both liquid and vapor.

The relation outlined above may also be stated thus: The weight of a unit volume of vapor at the condensation temperature is inversely proportional to the heat of vaporization. That is, equal volumes of vapor of unassociated substances at their condensation temperatures produce equal quantities of heat in condensing to liquids at the same temperature. For the fifteen substances given above we have an average of 257 calories for one liter of vapor condensing.

It may be well to note here that the relation is an absolute one and is independent of any theory. It will be seen in the sequel, however, that it is in full accord with the kinetic molecular hypothesis.

2. In vapors at their condensation temperatures the heats of vaporization are directly proportional to the squares of the velocities of the molecules. The velocity of the molecules may be calculated by substituting the known values in the formula $S = \sqrt{\frac{3pvT}{273mn}}$, where $S$ is the velocity, $p$ the pressure, $v$ the gram-molecular volume, $T$ the condensation temperature (absolute), and $mn$ the gram-molecular weight. The formula is derived from the kinetic molecular hypothesis

and a discussion of it may be found in Walker's "Physical Chemistry,' chapter X.

The above relation is expressed by the formula $\frac{S^2}{\lambda} = C$, where $S$ is the velocity of the molecules, $\lambda$ the heat of vaporization, and $C$ a constant.

The constants for some substances are shown in the following table:

| | S (Meters per second) | $\lambda$ | C |
|---|---|---|---|
| Ether | 100.9 | 86.00 | 118.2 |
| Benzene | 106.1 | 93.5 | 125.0 |
| Carbon bisulphide | 101.4 | 86.7 | 118.6 |
| Ethyl acetate | 98.7 | 83.05 | 117.3 |
| Chloroform | 83.3 | 58.5 | 118.0 |
| Mercury | 85.49 | 62.0 | 117.9 |
| Carbon tetrachloride | 74.04 | 46.35 | 118.2 |
| Ethylene oxide | 127.80 | 138.6 | 118.0 |
| Diethylamine | 104.50 | 91.0 | 120.4 |

As previously noted, Trouton found that the product of molecular weight and heat of vaporization is proportional to the absolute temperature of the boiling point. As shown above, the square of the velocity of the molecules is proportional to heat of vaporization. It therefore follows that the product of molecular weight and the square of the velocity is proportional to the absolute temperature of the boiling point. We have the equation

$$\frac{MS^2/2}{T} = C$$

This equation is true for the substances given in the last table and for other substances not associated. We may say, then, that the molecular kinetic energy of a vapor at the condensation point is proportional to the absolute temperature.

Trouton points out that the molecular heat of vaporization is proportional to the absolute temperature of the boiling point, and Walden has shown that the molecular cohesion is proportional to the same constant, so that we have molecular kinetic energy of the vapor, molecular cohesion of the liquid, and molecular heat of vaporization mutually proportional, and for a given substance specific cohesion in the liquid is proportional to the square of the velocity of the molecules of the vapor at the transition temperature.

3. The quantity of heat required to vaporize a unit volume of a liquid at the boiling temperature is directly proportional to the relative number of molecules, in the unit volume of liquid, and to the absolute temperature. We have the equation

$$\frac{H}{nT}=C$$

where $H$ is the heat required to vaporize a unit volume of liquid, $n$ the relative number of molecules in that volume, and $T$ the absolute temperature at the boiling point. If we choose 1 cc. as the unit volume, $H$ is the product of the density, $d$, and the heat of vaporization, $\lambda$; $n$ is found by dividing the density, $d$, by the molecular weight $m$.

The following table shows the relation for several substances:

| | $d\lambda = H$ | $d/M = n$ | $T$ | $C$ |
|---|---|---|---|---|
| Benzene | 76.67 | 0.01052 | 353.0 | 20.646 |
| Chloroform | 82.37 | 0.01178 | 334.0 | 20.877 |
| Ethyl acetate | 69.96 | 0.00956 | 350.0 | 20.900 |
| Methyl butyrate | 63.31 | 0.00819 | 375.0 | 20.624 |
| Carbon bisulphide | 102.79 | 0.0161 | 319.0 | 20.140 |
| Carbon tetrachloride | 99.39 | 0.00973 | 349.7 | 20.410 |
| Phosphorus trichloride | 77.18 | 0.0108 | 349.0 | 20.457 |
| Diethylamine | 60.90 | 0.00917 | 329.0 | 20.495 |

4. In the case of isomers we have the equation $\frac{d}{T} = C$.

This relation for several sets of isomers is shown below:

| | $d$ (at boiling point) | $T$ | $C$ |
|---|---|---|---|
| Methyl butyrate | 0.8190 | 375.0 | 0.002184 |
| Ethyl propionate | 0.8165 | 372.0 | 0.002192 |
| Propyl bromide | 1.287 | 344.0 | 0.003743 |
| Isopropyl bromide | 1.241 | 333.0 | 0.003727 |
| Ethyl acetate | 0.8424 | 350.0 | 0.002405 |
| Methyl propionate | 0.8489 | 353.0 | 0.002406 |
| Propyl formate | 0.8435 | 351.0 | 0.002414 |
| Ethylene chloride | 1.165 | 356.6 | 0.003268 |
| Ethylidene chloride | 1.093 | 333.0 | 0.003284 |

Kopp's observation that the densities of isomeric compounds at the boiling temperature are equal has been found not strictly true. The relation noted above is, in the case of many pairs of isomeric compounds, quite close.

5. The temperature of a boiling liquid is an inverse function of the relative size of the molecules and a direct function of molecular weight and of the square root of the number of atoms in the molecule.

We have the equation $\frac{bT}{M\sqrt{n}} = C$ in which $b$ has the same value as in the equation of van der Waals, $T$ is the absolute temperature, $M$ is the molecular weight, and $n$ the number of atoms in the molecule.

In the following table the relation is given for some substances, but there are a number of exceptions. The constants given in this table may be criticized as being very divergent, but it should be remembered that the term $b$ depends in value upon critical temperature and critical pressure, and that data for critical pressure given by different investigators sometimes vary largely. For benzene, as an example, the value of $C$ in the above equation is 0.00558 or 0.00669 according to the data used. With such divergence for one substance it is not surprising to find an equal and sometimes a greater divergence in the value of the constants when a number of substances are compared:

| | $b$ (detd. by Sajoschewsky) | $T$ | $M$ | $n$ | $C$ |
|---|---|---|---|---|---|
| Ether | 0.005745 | 307.6 | 74.08 | 15 | 0.00618 |
| Benzene | 0.005121 | 353.0 | 78.048 | 12 | 0.00669 |
| Chloroform | 0.004450 | 335 | 119.358 | 5 | 0.00558 |
| Ethyl acetate | 0.005551 | 350.0 | 88.064 | 14 | 0.00590 |
| Ethyl chloride | 0.003966 | 285.5 | 64.49 | 8 | 0.00622 |
| Ethyl formate | 0.004729 | 326.5 | 74.048 | 11 | 0.00627 |
| Methyl acetate | 0.003997 | 329.3 | 74.048 | 11 | 0.00620 |
| | $b$ (detd. by Nadejdine) | | | | |
| Ethyl acetate | 0.006034 | 350.0 | 88.064 | 14 | 0.00642 |
| Ethyl butyrate | 0.008567 | 392.0 | 116.096 | 20 | 0.00647 |
| Ethylene chloride | 0.004850 | 357.0 | 98.932 | 8 | 0.00619 |
| Ethylidene chloride | 0.004790 | 333.1 | 98.932 | 8 | 0.00571 |

| | *b* (detd. by Nadejdine) | *T* | *M* | *n* | *C* |
|---|---|---|---|---|---|
| Isobutyl acetate | 0.008185 | 389.5 | 116.096 | 20 | 0.00620 |
| Methyl acetate | 0.004870 | 329.3 | 74.048 | 11 | 0.00654 |
| Isoamylene | 0.006274 | 294.0 | 70.08 | 15 | 0.00680 |
| Methyl formate | 0.003602 | 305.5 | 60.032 | 8 | 0.00648 |
| Methyl propionate | 0.006070 | 352.5 | 88.064 | 14 | 0.00650 |
| Methylethyl ether | 0.004364 | 284.0 | 60.064 | 12 | 0.00596 |
| | *b* (detd. by Young) | | | | |
| Ether | 0.006011 | 307.6 | 74.08 | 15 | 0.00645 |
| Ethyl formate | 0.004971 | 326.5 | 74.048 | 11 | 0.00661 |
| Brombenzene | 0.006880 | 428.0 | 157.0 | 12 | 0.00542 |
| Chlorbenzene | 0.006496 | 405.0 | 112.49 | 12 | 0.00676 |
| Carbon tetrachloride | 0.005663 | 349.0 | 153.8 | 5 | 0.00575 |
| Diisopropyl | 0.007443 | 331.0 | 86.112 | 20 | 0.00641 |
| Heptane | 0.009201 | 371.4 | 100.128 | 23 | 0.00746 |
| Hexane | 0.007747 | 344.0 | 86.112 | 20 | 0.00748 |
| Octane | 0.010571 | 398.5 | 114.144 | 26 | 0.00725 |
| Pentane | 0.006518 | 311.0 | 72.096 | 17 | 0.00681 |
| Isopentane | 0.006408 | 303.0 | 72.096 | 17 | 0.00654 |
| Ethyl isobutyrate | 0.008410 | 383.0 | 116.096 | 20 | 0.00621 |
| | *b* (detd. by Vincent and Chappuis) | | | | |
| Ethylamine | 0.003122 | 291.0 | 45.096 | 10 | 0.00637 |
| Diethylamine | 0.005598 | 329.0 | 73.128 | 16 | 0.00631 |
| Dimethylamine | 0.003565 | 280.2 | 45.096 | 10 | 0.00702 |
| Dipropylamine | 0.008124 | 383.0 | 101.16 | 22 | 0.00657 |
| Methylamine | 0.002722 | 267.0 | 31.08 | 7 | 0.00886 |
| Propylamine | 0.004496 | 322.0 | 59.112 | 13 | 0.00680 |
| Triethylamine | 0.008176 | 362.0 | 101.16 | 22 | 0.00625 |
| Trimethylamine | 0.004841 | 276.5 | 59.112 | 13 | 0.00629 |
| | *b* (detd. by Dewar) | | | | |
| Ethylene | 0.002540 | 168.0 | 28.032 | 6 | 0.00626 |
| Cyanogen | 0.002900 | 252.0 | 52.08 | 4 | 0.00716 |

## CONCLUSION

Heat of vaporization has been variously explained, some claiming that the heat was required merely to cause the molecules to occupy a greater space in the gaseous condition, and others holding that the heat is responsible not only for greater volume but for intramolecular work as well. While a complete explanation is not offered in this paper, some remarks may be of value.

When a substance passes from the liquid to the gaseous condition a part of the heat is of course used in overcoming cohesion and giving the molecules sufficient kinetic energy to balance the atmospheric pressure. There is no question as to this point. In considering the matter of intramolecular work, however, there is a variety of opinions.

Pictet showed that at the boiling point cohesion is constant. Walden found that molecular cohesion is proportional to absolute temperature. Trouton showed that molecular heat of vaporization is proportional to absolute temperature. It has been shown in this paper that heat of vaporization is directly proportional to the velocity of the molecules in the gaseous condition at the transition temperature, and that molecular kinetic energy is proportional to absolute temperature. We have, then, molecular cohesion, molecular kinetic energy, and molecular heat of vaporization mutually proportional. Since we believe that velocity of molecules and molecular kinetic energy are independent of molecular complexity, and since we have no evidence that cohesion is affected by molecular complexity, we must conclude that molecular heat of vaporization is independent of molecular complexity.

It has been shown in this paper that the weight of a unit volume of a vapor at the transition temperature is inversely proportional to the heat of vaporization. Since the weight of a volume of a gas depends upon the pressure, temperature, and molecular weight it follows that molecular complexity is here of no effect. It has also been shown above that in a unit volume of liquid at the transition temperature, the heat required to vaporize it is proportional to the number of molecules and to the absolute temperature. Again, it is seen that complexity of molecules has no effect upon heat of vaporization.

Since, therefore, various molecules of different degrees of complexity show the same general behavior where heat of vaporization is involved, we may conclude that none of the heat of vaporization is required for intramolecular work, but that all is used in overcoming cohesion and in giving the molecules sufficient kinetic energy to balance the pressure.

In determining the boiling temperature, however, the size, weight, and complexity of molecules are all important factors. A liquid made up of heavy, small, and complex molecules will boil at a higher temperature than one made up of molecules lighter, larger, or less complex.

## SUMMARY

1. The volume of a unit weight of a vapor produced from a boiling liquid is proportional to the heat of vaporization. In other words, equal quantities of heat applied to liquids at their transition temperatures will produce equal volumes of vapor at these temperatures.

2. In vapors at their transition temperatures the heat of vaporization is proportional to the square of the velocity of the molecules and the molecular kinetic energy is proportional to the absolute temperature.

3. The quantity of heat required to vaporize a unit volume of a liquid at the transition temperature is directly proportional to the number of molecules in a unit volume and to the absolute temperature.

4. In the case of isomers the absolute temperature of the boiling point is proportional to the density of the liquid at the boiling point.

5. The absolute temperature of the boiling point is inversely proportional to the relative size of the molecules and directly proportional to the molecular weight and to the square root of the number of atoms in the molecule.

6. The conclusion is reached that the boiling point of a liquid is a function of size, weight, and complexity of molecules, but that heat of vaporization is not concerned in molecular complexity, except association, or in intramolecular work.

LABORATORY OF THE MISSISSIPPI
A. & M. COLLEGE.

# REVIEWS

**ZERKLEINERUNGSVORRICHTUNGEN UND MAHLANLAGEN.** Von CARL NASKE, Zivilingenieur. Mit 257 Figuren im Text. Chemische Technologie in Einzeldarstellungen, herausgegeben von FERDINAND FISCHER. Leipzig: Verlag von Otto Spamer. 1911. S. x + 235. Preis, geh., M. 13.50; geb., M. 15.

This book has been written especially for the industrial chemist but will be found of value for the engineer. The author has made use of prominent authorities and catalogues for obtaining descriptions of breaking and comminuting machines of all kinds and for all purposes, together with other necessary apparatus for handling the ground products. With the limits set the description of any one machine is necessarily not detailed, but brief and to the point.

The following list indicates the range of subjects covered: Breakers, rolls, Chili mills, cone mills, impact machines or disintegrators, stamps of gravity, steam and hydraulic types, grinders, roller mills, ball mills, tube mills, screens of bar, trommel and shaking types, air separators of various types, dust collection by settling chambers, dry filters (bag houses), centrifugal action, water spray and wet filters, storage and packing products, individual plants for phosphate, superphosphate, paints, sal ammoniac, hyposulphite, dolomite, common salt, clay for earthenware, cement, road material, drugs and spices.

Some machines of doubtful value are bound to be included in a book of this kind but the author has done his work so well that the reader may well overlook any minor fault of this nature.

CHARLES E. LOCKE.

**ALLEN'S COMMERCIAL ORGANIC ANALYSIS.** Vol. IV. Resins, India-Rubber, Rubber Substitutes and Gutta-Percha, Hydrocarbons of Essential Oils, Ketones of Essential Oils, Volatile or Essential Oils, Special Characters of Essential Oils, Tables of Essential Oils. By the editors and the following contributors: M. BENNETT BLACKLER, E. W. LEWIS, T. MARTIN LOWRY, ERNEST C. PARRY, HENRY LEFFMANN, CHARLES H. LAWALL. Fourth edition. Entirely rewritten. Edited by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, S.B. Philadelphia: P. Blakiston's Son & Co. 1911. pp. viii + 466. Price, $5.00.

The chapter upon resins (103 pp.) gives a clear, concise and satisfactory account of the more important of these substances, together with the oleoresins and balsams. Due acknowledgment is made of the debt chemists owe to Tshirch and Dieterich.

The chapter on rubber (58 pp.) is more valuable for information as to manufactured products and their uses than for analytical directions. Weber is very closely followed. The remainder of the book is devoted to the essential oils, their origin, properties and adulterants being given. Careful attention has been paid to the recent methods and literature.

The availability of the work would be much increased by a more complete index, including a list of authors.

The volume may be commended to all those interested. No technical chemist's library is complete without one or more volumes of "Allen."

A. H. GILL.

DIE DIREKTE EINFÜHRUNG VON SUBSTITUENTEN IN DEN BENZOLKERN. Ein Beitrag zur Lösung des Substitutionsproblems in aromatischen Verbindungen, Kritische Literaturübersicht und experimentelle Untersuchungen. Von DR. A. F. HOLLEMAN, ord. Professor der Chemie an der Universität Amsterdam. Mit zahlreichen Figuren. Leipzig: Veit und Comp. 1910. S. vi + 516. Preis: geh., M. 20; geb., M. 23.

In the preface of this valuable book Professor Holleman gives his reasons for publishing it:

"A review of the experimental work and theories on the direct introduction of substituents into the benzene nucleus has to my knowledge not yet been published. As I have been engaged for several years in working on this problem I resolved to undertake such a review and to incorporate my own investigations at the proper places. For my own work it was necessary to study over a thousand papers, as I was desirous, as far as possible, of giving a complete review of the literature of the subject. In doing this I have not merely compiled the work done, but have also subjected the papers to criticism, so far as this was possible without repeating the experiments therein described." It is certainly a matter for congratulation that this task has been undertaken by such a competent authority in this field as Professor Holleman, and all chemists owe him a debt of gratitude for the excellent manner in which the work has been done.

Anyone who has worked in this field of organic chemistry or who is familiar with the literature of the subject will indorse this statement of the author, also found in the preface:

"A cursory inspection of this book will show at once that even in the case of many quite simple reactions it has not yet been determined with sufficient accuracy qualitatively what isomers are formed under certain definite conditions, let alone the relative quantities of these isomers which are formed simultaneously. The conviction forces itself upon us that a complete revision of all work on the direct introduction of substituents into the benzene molecule which already contains one or more groups, not only qualitatively but especially quantitatively, is essential if this problem is to be seriously attacked."

This is shown very clearly in an article just published by the author and some of his pupils[1] entitled "Quantitative Investigations on the Nitrating of Aniline," in which he shows that the conclusions stated in this book regarding the nitration of aniline and its derivatives are not correct. He had assumed, from the work of others, that the direct nitration (that is, the direct replacement of hydrogen of benzene by the group $NO_2$) of aniline sulphate gave only the *meta* product, while the indirect nitration (through the intermediate formation of phenylnitramine) led to *para* and *ortho* derivatives. The investigation above referred to, however, proves that this hypothesis is not correct. For, in nitrating aniline in sulphuric acid, in which case the aniline is undoubtedly nitrated as sulphate, there is formed, in addition to the *meta* compound, a considerable quantity of *para*nitraniline also, and only very little of the *ortho* isomer. On the basis of the results of this investigation Professor Holleman now formulates the reaction as follows:

1. In the nitration of aniline and its derivatives, as well as in the introduction of halogens, the main product is the *para* compound, together with certain quantities of the *ortho* isomer.

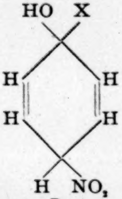
2. Two circumstances may modify this result: (*a*) the formation of sulphate and the accumulation of acid residues in the group $NH_2$, whereby the *meta*nitro product is formed; (*b*) indirect substitution whereby mainly the *ortho*nitro compound results.

The first chapter of the book takes up the direct introduction of one substituent into the unsubstituted benzene nucleus. The second is devoted to the quantitative estimation of isomers in the presence of one another and the determination of the series to which the bisubstitution products belong. In the third chapter the direct introduction of a second substituent into a monosubstituted benzene is considered, and in the fourth chapter the author discusses the results and gives some theoretical observations. In the fifth chapter the introduction of a third substituent into a disubstituted benzene is taken up, and the sixth is devoted to a discussion of the results, both qualitative and quantitative. The seventh and last chapter is given up to a discussion of the melting-point curves of binary mixtures and the quantitative analysis of mixtures of three isomers by means of the melting-point figure of ternary mixtures.

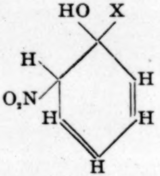
---

[1] Ber. d. Chem. Ges., **44**, 704 (1911).

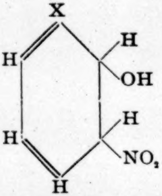
In chapter six the author develops his own views on the mechanism of substitution. Starting with Kekulé's benzene formula, he assumes that substitution in the benzene ring is preceded by the formation of an addition product. For example, if the compound $C_6H_5X$ is nitrated one or more of the three addition products



Para.



Ortho.



Meta.

first formed lose water and the less stable ring with two double bonds goes back to the more stable benzene ring. Which of these three addition products will be formed, that is, which type of substitution product will result, will be determined by the velocity of the reaction. If the group X accelerates the reaction, substitution will take place in the para and ortho positions and exclusively in these positions when X exerts a large accelerating influence. If the accelerating influence of X is not so great, then certain quantities of the meta compound may be formed. For example, phenol gives on nitration only para- and orthonitrophenol, while toluene yields some of the meta compound in addition to the other two. If X has a retarding influence then the addition at the double bond 2,3 predominates, the consequence of which is that the meta compound will be the main product.

For anyone who works in this field of organic chemistry this book will be absolutely indispensable and even the average chemist will find here material that will fully repay all the time he devotes to it. W. R. O.

**ELEKTRISCHE DOPPELBRECHUNG DER KOHLENSTOFFVERBINDUNGEN.** Von DR. PHIL. RICHARD LEISER, aus Wien. Mit 15 als Anhang gedruckten Abbildungen. Abhandlungen der Deutschen Bunsen Gesellschaft für angewandte physikalische Chemie. Nr. 4. Halle a. S.: Druck und Verlag von Wilhelm Knapp. 1910. pp. 71. Price, M. 3.60.

In this monograph the author gives an account of a series of interesting experiments on the relation between the electrical double refraction and the chemical constitution of organic compounds. He bases his method of experimentation upon the well known observation made by Kerr in 1875 that if a layer of carbon disulphide is placed between two crossed Nicol prisms and is subjected to electric stress the plane of polarization is rotated. The experimental arrangements are too complicated to admit of a brief description, hence it must suffice to state that an optical system was devised which permitted the detection of a phase difference of $3 \times 10^{-5}\lambda$. With this apparatus the "Kerr Constants" of electrical double refraction of one hundred and fifty organic compounds were measured.

The constants of a few well known compounds are as follows:

| | |
|---|---|
| Propyl alcohol | —78.0 |
| Isopropyl alcohol | +73.0 |
| Benzene | 12.1 |
| Toluene | 24.3 |
| *o*-Xylene | 41.2 |
| *m*-Xylene | 24.4 |
| *p*-Xylene | 22.6 |
| Chloroform | —100.0 |
| Carbon tetrachloride | 2.3 |

These examples would seem to justify the author's claim: "Es dürfte sogar, nach den bisherigen Erfahrungen zu urteilen keine andere physikalische Eigenschaft so charakteristisch für die chemische Konstitution und daher so geeignet sein, daraus Schlüsse auf die Konstitution unbekannter Verbindungen zu ziehen, als die elektrische Doppelbrechung." The author has also sought to develop a new concept of the nature of electrical double refraction which differs fundamentally from the theory which is generally accepted.

The method described in this monograph, notwithstanding the somewhat elaborate and complex apparatus required, should prove of great value in helping to establish the constitutions of many compounds which at the present time are unsettled.

FREDERICK H. GETMAN.

THE ELECTRICAL NATURE OF MATTER AND RADIOACTIVITY. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. Second edition, completely revised. New York: D. Van Nostrand Co. 1910. pp. ix + 210. Price, $2.00.

The first edition of this book has already been reviewed in THIS JOURNAL.[1] The aim of this edition has been "to bring it up-to-date as far as matters of fundamental importance are concerned," otherwise it hardly needs an introduction to the chemical public.

---

[1] Vol. 36, p. 614.

There is surely no topic upon which the physical chemist is so often questioned by the laity as that which is included by the title of this book. In spite, however, of the general interest and fundamental scientific importance of these matters, but few have any direct experimental knowledge of them. This volume fills, therefore, a very general need for information which shall be concise, nonmathematical, and which shall explain clearly into just what sort of a thing the atom has evolved nowadays. The ability of the author to do this in a manner within the grasp of those without special training, and yet thoroughly scientific, is well known, so that this new edition will be welcomed by many.

In view of the accumulated evidence in favor of 225 as the atomic weight of radium, it seems rather strange that the long argument in favor of the higher value is still retained. There are occasional evidences of revision, such as the reference to work done in 1905 as "quite recent." On p. 95 the term "hardness" is used in a sense familiar only to workers with the X-ray tube. On p. 190 "radium" is printed where evidently "sodium" is intended, and on p. 197 we find "hydrogen sulphate." The liquefaction of helium occurred too late to be used in correcting the text on pp. 137 and 154 or else was neglected. A few such errors are, however, almost inevitable, and the volume remains, doubtless, the best semipopular text on the subject.

JOEL H. HILDEBRAND.

**TRAITÉ DE CHIMIE GÉNÉRALE.** Par W. NERNST, Professeur à l'Université et Directeur de l'Institut de Chimie Physique de l'Université de Berlin. Ouvrage traduit sur la 6e édition allemande par A. CORVISY, Professeur Agrégé des Sciences Physiques au Lycée Gay-Lussac, Professeur Suppléant à l'École de Médecine et de Pharmacie de Limoges. Première Partie: Propriétés Générales des Corps-Atome et Molécule. Paris: Librairie Scientifique A. Hermann et Fils. 1911. pp. 11 + 510. Price, Fr. 12.

The increasing number of German books being translated into French, and *vice versa*, gives gratifying evidence of the growing feeling of good will and mutual appreciation between the two nations. In his preface, Prof. Corvisy, the excellence of whose work as a translator is already known through his translation of Ladenburg's History of Chemistry, pays a graceful tribute to Prof. Nernst's book which, since its first appearance, has been a source of so much help and inspiration to all physical chemists. The volume under review covers the first 18 chapters of the "Theoretische Chemie." The original text of the 6th German edition has been closely followed, only a few changes in the interest of historical accuracy having been made at the suggestion of Prof. Nernst himself. French chemists are to be congratulated on having such an excellent translation placed at their disposal. C. A. R.

Qualitative Chemical Analysis, a Laboratory Guide. By Wilfred Welday Scott, A.M., Chief Chemist, Baldwin Locomotive Works, formerly Professor of Chemistry, Morningside College. Illustrated. New York: D. Van Nostrand Co. 1910. pp. xi + 165. Price, $1.50.

In this well-balanced manual the author gives 11 pages of the introduction to the application of physical chemistry to analysis, and a few pages to laboratory directions.

The greater part of the book is a systematic study of bases and acids; the order observed with each element is a brief mention of the important compounds, special tests, preliminary reactions, group separations, discussion of details of analytical methods, and a number of questions. A chapter on systematic analysis follows. The next chapter contains tables of reactions of acids and bases, followed by directions for preparing reagents and by a table of solubilities.

Professor Scott's book is admirable. The analytical methods employed are without exception the best. The discussions of methods are clear and thorough. E. R.